**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE AND TECHNOLOGY**

# SYNTHESIS AND CHARACTERISATION OF PES/ PCz COMPOSITE

**M.Sc. THESIS**

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**Department of Polymer Science and Technology**

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**MAY 2015**

**İSTANBUL TEKNİK UNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**

# PES/PCz KOMPOZİTİNİN SENTEZİ VE KARAKTERİZASYONU

**YÜKSEK LİSANS TEZİ**

**MEHMET AKİF KÜÇÜKKAYA**
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**Polimer Bilim ve Teknolojisi Bölümü**

**Polimer Bilim ve Teknolojisi Proğramı**

**Tez Danışmanı: Prof. Dr. Belkıs USTAMEHMETOĞLU**

**MAYIS 2015**

M.Akif KUCUKKAYA, a M.Sc. student of ITU Graduate School of Science and Technology student ID 515091037, successfully defended the thesis entitled “Synthesis and Characterization of PES/PCz Composite”, which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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**Prof. Dr. Esma SEZER**

Istanbul Technical University

***To my familiy and future,***

**FOREWORD**

I wish to thank at first place to my thsesis advisor Prof. Dr. Belkıs Ustamehmetoğlu for her expert guidance, motivation and support at all levels of this study. It was great pleasure for me to conduct this thesis under her supervision and to know her personally.

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MAY, 2015

M.Akif KUCUKKAYA

Metallurgy and Material Engineer

**TABLE OF CONTENTS**

**Page**

**ABBREVIATIONS**

| | |
|---|---|
| **CAN** | **:** Acetonitrile |
| **Ani** | **:** Aniline |
| **CAN** | **:** Cerium (IV) Ammonium Nitrate |
| **Cz** | **:** Carbazole |
| **DBSA** | **:** Dodecyl Benzene Sulphonic Acid |
| **DMA** | : Dynamical Mechanical Analysis |
| **DSC** | : Differential Scanning Calorimetry |
| **$FeCl_3$** | : Iron (III) Chloride |
| **FTIR** | : Fourier Transform Infrared Spectroscopy |
| **MEKF-R** | : Methyl Ethyl Ketone Formaldehyde Resin |
| **PANi** | : Polyaniline |
| **PCz** | : Polycarbazole |
| **PES** | : Polyester |
| **PET** | : Polyethylene terephthalate |
| **PPy** | : Polypyrrole |
| **PTSA** | : *p*-Toluenesulfonic acid |
| **Py** | : Pyrrole |
| **SEM** | : Scanning Electron Microscopy |

## LIST OF TABLES

**Page**

**LIST OF FIGURES**

**SYNTHESIS AND CHARACTERISATION OF PES/ PCz COMPOSITE**


## SUMMARY

In recent years, conductive polymers have been used in various field and become an important alternate instead of metals. This approach causes an increase in improvement regarding conductive polymers. Conductive polymers are used as body area network (BAN), antenna, sensor, electrode, cathode material obtained by coating onto PET and glass, electrocardiography (ECG), electromiyography (EMG), electromagnetic shielding applications in military and on the sports field. Conductive textiles are one of the applications of conductive polymers. Polypyrrole (PPy), polyaniline (PANi), polythiophene (PTh), polydioxythiophene(PEDOT):paratoluenesulphonicacid(PTSA), PEDOT:PSS copolymers and Poly(3-methyl thiophene) (P3MTh) nano application are within application of conductive polymers.

In this study, it is aimed to synthesize PCz by in situ polymerization onto polyester (PES) textile substrate with using different oxidants and solvents. Most studies have been focused on in situ polymerization to produce conductive textile since this method does not require the destruction of the substrate and provides reasonably good conductivity. The final form of PCz is that of a long conjugated backbone. The polymer has resonance structures. In this neutral state the polymer is not conducting and only becomes conducting when it is oxidized. $FeCl_3$ and CAN were used as oxidant. Acetonitrile (ACN), water and toluene was used as solvent. It was investigated the effects of different concentration of monomer, oxidant, solvent and polymerization time and also the order of immersion of Cz monomer and oxidant solutions to electrical conductivity. Electrical conductivities and capasitive values were measured by disc probe. PES/PCz composites were characterized by Color analysis, Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR), Dynamical Mechanical Analysis (DMA) methods. As a result, PCz was coated onto PES tekstile in the presence of $FeCl_3$ and PES/PCz composites were obtained with 0.32 Ω electrical resistance.

## PES/PCZ KOMPOZİTİNİN SENTEZİ VE KARAKTERİZASYONU


### ÖZET

İletken polimerler son yıllarda çeşitli alanlarda kullanılmaya başlamış ve metaller için önemli bir alternatif haline gelmişlerdir. Bu yaklaşım iletken polimer üzerinde yapılan geliştirme çalışmalarının artmasına sebep olmuştur. Polypyrrole (PPy), polyaniline (PANi), polythiophene (PTh), polycarbazole (PCz) polimerleri, polidioksitiyofen(PEDOT):politoluensülfonikasit(PTSA), PEDOT:PSS kopolimerleri ve Poly(3-metil tiyofen) (P3MTh) nano uygulaması iletken tekstil uygulamalarında yer almaktadır. İletken tekstiller body area network (BAN), anten, sensör, PET ve cam üzerine kaplanarak elde edilen katod malzemesi, elektrokardiogram (EKG), elektromiyografi (EMG), elektromanyetik kalkanlama uygulamaları ile askeri alanda, otomotiv sektöründe, sportif ve estetik amaçla kullanılmaktadır. İletken tekstiller iletken polimerlerin uygulama alanlarından bir tanesidir.

Son yıllarda tekstilin uygulama ve özelliklerindeki gelişmeler büyük dikkat çekmektedir. Bu özelliklerden bir tanesi elektriksel iletkenlik özelliğidir. Çok sayıda iletken tekstil uygulamaları görülmektedir. Örneğin gaz sensörü, biyomekanikal sensör, elektroterapi, ısıtma cihazı, mikrodalga zayıflama, sensörler, elektromanyetik koruma, toz ve bakteri önleme, statik yük boşaltma, görüntüleme, bilgi transferi sağlama gibi konularda gerekli endüstriyel ürünlerin üretilmesinde büyük rol oynamaktadır.

Bu çalışmada PCz' nin PES üzerine farklı çözelti ortamlarında ve farklı dopant kullanılarak in situ polimerizasyon tekniği kullanılarak sentezlendi. Bir çok çalışma in situ polimerizasyon üzerine yoğunlaşmıştır. Çünkü bu metod tekstil üzerinde bir tahribata sebep vermeyip, iyi bir iletkenlik sağlamaktadır. PCz, uzun konjuge bir zincire ve rezonans bir yapıya sahiptir. PCz nötr durumda elektiriği iletemez, oksidasyon ile iletkenlik özelliği kazanır. Öte yandan, PES tekstil endüstrisinde en yaygın kullanılan polimerlerden biridir. Çünkü yüksek mukavvemet, düşük nem absorbsiyonu ve çekmeye karşı direnç özeliklerine sahiptir. PES in en büyük avantajı

geri dönüşüm özelliğinin olmasıdır. Tekstilin monomer absorbsiyonunu artırabilmek için DBSA yüzey aktif olarak kullanılmıştır. Polimerizasyon sırasında değişik konsantrasyonlarda monomer, oksidant, çözücü kullanıldı ve polimerizasyon sürelerinin elektriksel direnç üzerine etkileri incelenmiştir. Oksidant olarak $FeCl_3$ ve CAN kullanılmıştır. Oksidant tarafından serbest bırakılan $Cl^-$ iyonları PCz 'in doplanmış formu için doplama ajanı olarak rol oynar.

Elektiriksel direnci ve kapasitans değerleri disk prop cihazıyla ölçülmüştür. Renk analizi, Tarama Elektron Mikroskopu (SEM), Infrared spektroskopisi (FT-IR), Dinamik mekanik analiz (DMA) gibi metodlarla karakterize edilmiştir.

Cz absorbsiyonun daha iyi olabilmesi için ağırlığı ölçülüp kayıt edilen kaplanmamış tekstilin su ve DBSA dan oluşan ortam içerisinde 30 dk, sonra ACN ve DBSA dan oluşan ortam içerisinde 30 dk. bekletilmiştir. Daha sonra Cz'ün tekstil üzerine birikmesini sağlamak için 1 saat kadar Cz monomeri ve ACN den oluşan ortam içerisinde bekletilmiştir. Bu süre sonunda tekstil $FeCl_3$ ve ACN den oluşan ortam içerisinde 10 dk bekletilmiştir. Tekstilin Cz ve $FeCl_3$ ortamları arasında ki değişimi 8 defa tekrarlanmıştır. Son olarak kaplanan tekstil ACN ile yıkanarak oda sıcaklığında kurutulmaya bırakılmıştır. PES/PCz kompozitinin ağırlığı ölçülmüştür ve verim hesabı yapılmıştır.

PES/PCz kompozitinin elektiriksel direnci üzerine Cz, $FeCl_3$, CAN konsantrasyonu , yüzey aktif maddesi, solvent etkisi ve polimerizasyon süresi etkileri incelenmiştir.

CAN verimliliği tekstil üzerine birikmekten çok çözeltide polimerizasyon oluşturmak için çok fazla. Oksidasyon potensiyeli CAN a göre daha düşük olan $FeCl_3$ durumunda, PCz tekstil üzerine iyi bir elektirik iletkenlik özelliğine sahip olarak kaplanmıştır. Bu yüzden $FeCl_3$ oksidant olarak PES üzerine Cz polimerizasyonunda kullanılmıştır.

Solvent etkisi toluene, CAN ve su kullanılarak araştırılmıştır. ACN durumunda en yüksek iletkenlik elde edilmiştir.

Yüzey aktif tekstilin ıslanmasını artırmak için kullanılmaktadır. DBSA ve PTSA yüzey aktif olarak kullanılmıştır. En yüksek iletkenlik DBSA ile elde edilmiştir.

Polimerizasyon süresi elektirksel direnci etkiler. Uzun polimerizasyon süresi düşük elektiriksel dirence sebep olduğu elde edilmiştir.

Tekstil üzerine kaplanmış iletken polimerler farklı renklere sahiptir ve renk analizi bu farkı karakterize etmek için kullanılmıştır.

Dinamik mekanik analiz (DMA) bir malzemenin sıcaklık ve uygulanan yük frekansına bağlı olarak eleastik modülü, damping ve enerji kayıbı gibi karakteristik özelliklerini hesaplar. DMA ölçümlerinde kaplanmamış PES ve PES/PCz kompoziti benzer mekanik davranış göstermiştir. Fakat PES/PCz durumunda, elastite modülü PES durumuna göre daha fazladır.

İnfrared (IR) spektroskopi moleküllerin vibrasyonuna dayalı bir tekniktir. Bir IR spectrumu bir numuneden ışın demeti geçirilmesi ve absorblanan ışın demetinin fraksiyonun belirlenmesidir. Her pikte görülen abroblanan enerji bir numune molekülünün vibrasyon frekansına karşılık gelmektedir. FT-IR sonuçlarında, PES ve PCz/PES kompoziti için C-H bağı 1012 $cm^{-1}$ ve 720 $cm^{-1}$ piklerinde ve C=C bağı 1622 $cm^{-1}$ pikinde görülmüştür.

Tarama electron miksorkopu (SEM) polimerler hakkında çok fazla detay verir. SEM numune üzerinden yansıyan elektronları görüntüler. Bu görüntülen yüzey morfolojisi veya partükül boyutu hakkında çalışmak için kullanılır. Cz konsantrasyonunda artış poliester üzerinde polimer artışına sebep olmaktadır. FT-IR daki güçlü pikler ve SEM ölçümlerindeki daha düz yüzey bu olayı desteklemektedir. PES/PCz kompozitlerinin çekme modülü, kaplanmamış PES e göre daha yüksektir ve tekstil üzerindeki boşlukların kaplama işlemi süresince kapanmasıyla doldurulmasıyla açıklanabilir.

İletken malzemelerin direnci disk prob kulllanılarak ölçülmüştür. Tekstil malzemesinin fiber yapısından dolayı, 4 prob yerine disk prop kullanılmıştır. İletken teksitilin elektiriksel özelliği polimer iletkenliğine bağlıdır. Disk prop ayrıca kalınlık hakkında bilgi verir.

PES/PCz kompoziti için 0,01 M Cz konsantrasyon varlığında en yüksek iletkenlik değeri $5.9x10^{-5}$ olarak ölçülmüştür.

Sonuç olarak, PES' in iyi mekaniksel özelliği ve PCz 'in iletkenlik özelliği ile PES/PCz kompozitinin literatürde çeşitli iletken tekstillerin kullanıldığı alanlarda kullanılmaya adaydır.

## 1. INTRODUCTION

Macromolecules consisting of repeating molecules of the same chemical structure are called polymer (1) the ability of a material to carry electrical charge is called conductivity, organic macromolecules that have the ability to transmit electric charge are called conductive polymers (2-3).Conductive polymers are also called as synthetic metals because they have similar properties to metals and they are produced synthetically. Alan J.Heeger, Alan G.Mac Diarmid and Hideki Shirakawa won the Nobel Chemistry Award at year 2000 with the method they found and developed, polyacetylene doped with iodine by oxidation, at 1977 about conductive organic polymers that have a high conductivity (4). The nature of conducting polymers, doesn't just makes them conductive, but also electroactive. Uses of these polymers can be considered as making: electroluminescence, microelectronics, textiles, semiconductor chips, integrated circuits, light battery components, sensors, antistatic coating, and packaging. In addition, transistors, television screens and sun panels, heat generation and such areas like electromagnetic shielding, also the electrical indicators that uses electroactivity, the light emitting devices (LEDs) and biosensor-type materials uses conductive polymers in their construction (2-3). Nowadays it is known that a large number of conductive polymers are used like PPy, PCz (5), PANi (6), polythiophene (PTh) (7) even some of their commercial productions are being made. But besides their weak mechanic properties, conductive polymers being in soluble and in dissoluble limits those being shaped for the intended purpose (8).

In literature Polymer conductivies were reported as $1.3 \times 10^{-2}$ S/cm (13) which synthesized with electrochemical polymerization method has higher conductivity than polymer $8.2 \times 10^{-5}$ S/cm (5). which synthesized with chemical polymerization method.

Textiles are one of the oldest polymeric materials known to mankind. In the early 1900s the development of composites made with cotton cloth and phenolic resin has increased the importance of these materials. Nowadays, textiles play a big role in a

lot of engineering supplies that includes polymers, ceramics and metals. Because of the fast improvements on the electric, particularly on the electronic industries started to need flexible, conductive and semi-conductive materials. On the other hand, a conductive textile means a fabric capable of transmitting electricity, with the spraying of conductive polymers, filaments can be formed or weaving it to make a textile or other different methods can be used to make a monomer polymerize onto an insulating textile to form a conductive homogeneous layer in order to form conductive textile. This, with the wide range of structural and mechanical properties of the textile allows the combination of electrical properties of the conductive polymers. The thickness of the conductive film depends on the synthesis time of the monomer and the oxidant concentration, it's valued in microns. The obtained (textile / conductive polymer) composites provide many processing problems to be overcomed in producing pure form of conductive polymer and powerful, flexible, sometimes elastic, conductive composites are found in larger usage areas.

With the mechanical properties of flexible and elastic textiles, the advantages of the electrical properties and biocompatibility being merged allows its composites to be used in such areas as electromagnetic shielding interface, broadband microwave absorption, static charge dissipation, biomedical and tissue engineering. Such fabrics can be used in military applications, the heating element, smart wearable devices in the preparation of materials for training and rehabilitation (9-14) and PAni (15) can be considered as the other most used polymers to form conductive textiles. One of the most widely used conductive polymer that has a good capacitive property is PCz (12) However, in the literature, there hasn't been a report about this polymer being used in conductive textiles.

In this study, PCz onto PES textile carries was synthesized for the first time. The PES/PCz composite textile was made under different monomer concentrations and $FeCl_3$ as oxidant, the optimum conditions were determined from the data which was obtained by conductivity measurements. The method that gave the highest conductivity was determined as main method. The results for the characterization, surface resistance, color analysis, SEM, FTIR, DMA were investigated and compared to the results of PES alone, PES/PCz under the same conditions.

## 2. THEORY

### 2.1 Polymers

Use of natural polymers by humans goes back to the prehistoric age. Well-known examples of polymer sources identified at that time include cotton (for cellulose), wood (for cellulose, hemi cellulose, and lignin), horn (for keratin) and hevea sap (for natural rubber, i.e., cis-1,4-polyisoprene).

The early 1900s saw the birth of the first truly synthetic polymers to be patented, first Bakelite in 1907, made from phenol and formaldehyde, and then poly(vinyl chloride) in 1914. During 1930s, shortly after the acceptance of the macromolecule concept, chemist learned how to produce many synthetic polymers including polystyrene, polyethylene, poly(methyl methacrylate), acrylics, polyamides, epoxy resins, silicones, and so on. During and just after World war II, both synthesis and industrial production of polymers grew exponentially. Most of these polymers, such polyamides for instance, are still widely used today. The 1950s are the beginning of what is sometimes called ‘’ the plastic age’’ (17).

Polymers are macromolecules built up by the linking together of large numbers of much smaller molecules. The small molecules that combine with each other to form polymer molecules are termed monomers, and the reactions by which they combine are termed polymerizations. There may be thousands, or more monomer molecules linked together in a polymer molecule (18).

### 2.2 Conductive Polymers

Polymers are normally used in electrical and electronic applications as insulators, where advantage is taken of their high resistivities and good dielectric performances. Typical examples of this type of application include cable sheathing, capacitor films, printed circuit substrates, and various encapsulants and conformal protective coatings. However, polymers are also widely exploited because of their other advantageous properties, including mechanical strength, flexibility, stability, low

cost and ease of processing, and it is the promise of combining these properties with electrical conductivity that has prompted the now great interest in conductive polymers (19).

The impact of the field on science in general was recognized in 2000 by the awarding of the Nobel Prize for chemistry to the discoverers of conducting polymers: Alan MacDiramid, Alan Heeger and Hideki Shirakawa (20).

Conducting electroactive polymers (CEPs) such as PPy, PCz (17), PTh, PANi, and sulfonated polyaniline are complex, dynamic structures that captivate the imagination of those of us involved in intelligent material research (22-26).

In recent years, an extensive development of conducting polymers in industry has made a new field of study in connection with some electrical applications of polymers such as saving information, sensors, catalysts and polymeric electrodes (27).

Figure 2.1 shows the main areas of interest for papers published on CEPs over the past 25 years, with almost half of the publications related to the synthesis of new types of CEPs or modifications to existing CEPs.

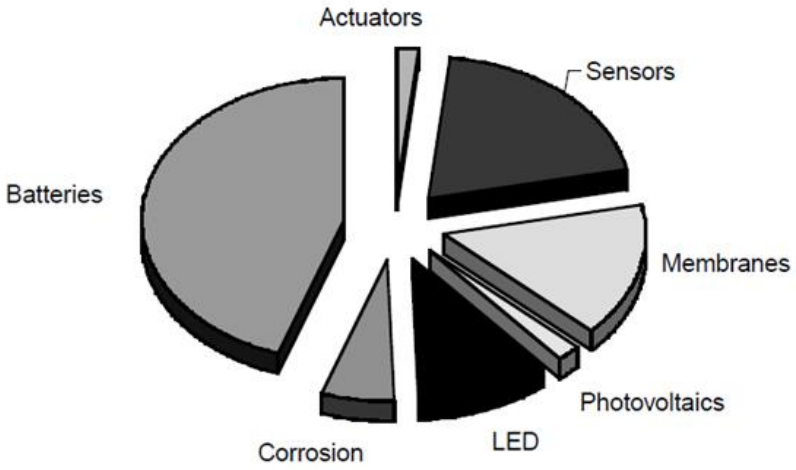
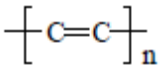
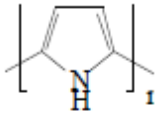
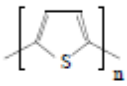
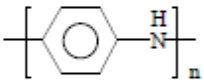
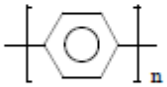
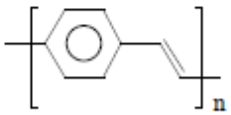
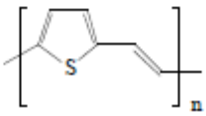
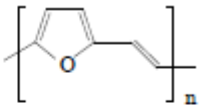
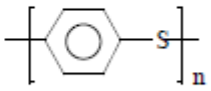
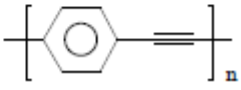
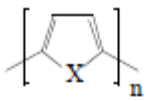
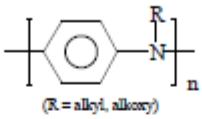
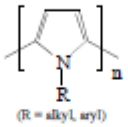
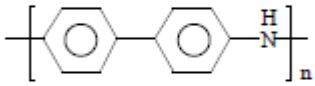
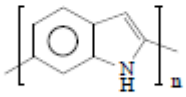
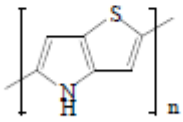
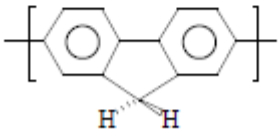
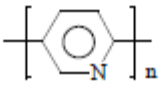



**Figure 2.1:** Scientific papers published on conducting polymers in the last 10 years categorized into applications.

Table 2.1 shows most common conductive polymers and their structures. A wide range of CEPs is available.

**Table 2.1:** Typical Conducting Polymer Structures

| Name | Structure |
|---|---|
| Polyacetylene (PAc) |  |
| Polypyrrole (PPy) |  |
| Polythiophene (PTh) |  |
| Polyaniline (PAn) |  |
| Poly(para-phenylene) (PPP) |  |
| Poly(phenylene-vinylene) (PPV) |  |
| Poly(thienylene-vinylene) (PTV) |  |
| Poly(furylene-vinylene) (PFV) |  |
| Poly(phenylenesulfide) (PPS) |  |
| Poly(phenylene ethynylene) (PPE) |  |

| | |
|---|---|
| Polyseleneophene (X = Se)<br>Polyfuran (X = O) |  |
| Poly(N-substituted aniline)s |  |
| Poly(N-substituted pyrrole)s |  |
| Poly(diphenylamine) |  |
| Poly(indole) |  |
| Poly(thieno[3,2-b]pyrrole) |  |
| Poly(fluorene) |  |
| Polypyridine |  |

### 2.2.1 Polycarbazole (PCz)

Cz was discovered in 1872 in the crude anthrance fraction of cool tar (28). Cz is a well-known hole-transporting and electroluminescent unit. Polymers containing Cz moieties either in the main or side chains have attracted much attention because of their unique properties, which allow for various applications (29-30). For example, opto-electronic devices (31), solar cells (32), dye (33).

Among the polymeric structures, the Cz unit is very advantageous because of very cheap starting material, fully aromatic unit providing a better chemical and environmental stability, nitrogen atom can be easily substituted with a wide variety of functional groups to and lastly it possesses a bridged biphenyl unit resulting in materials with a lower band gap than traditional poly(p-phenylene)s., good

electrolumescent and electron donor. A π-π electron system along its backbone imparts rigidity to the PCz, and therefore, makes it infusible and difficult to process. For this reason, it was not initially significantly used in devices compared to other conducting polymers like PTh. However, recent advances in synthesis methods have focused interest in PCz (34). It can be seen structure of PCz at figure 2.2.

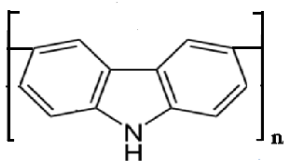


**Figure 2.2:** Chemical structure of PCz

## 2.3 Polyester (PES)

The term 'polyester' is applied to polymers containing ester groups in their main polymeric chain. PES are derived from a polycondensation reaction between dicarboxylic acids and diols. The chemical formula of PES is shown at figure 2.3.

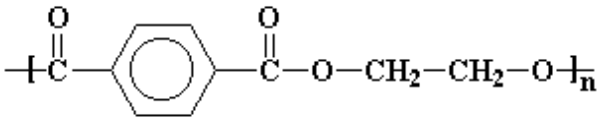


**Figure 2.3 :** Chemical structure of PES

PES can be broadly classified into two types:

**1.** Thermoplastic PES, which consist of fibre-forming, film-forming and engineering application polymers such as PET.

**2.** Thermoset PES which are basically unsaturated PES resins (liquid form) that upon curing form highly cross-linked structures (solid). They are widely used as a matrix for preparation of fibre-reinforced composite materials to bind the fibrous structure together. The thermoplastic PES is the most widely used synthetic polymer.

Although many variants of PES are available, PES is very important for textiles and other commercial sectors. PES is also used for the manufacture of plastic bottles,

films, canoes, liquid crystal displays (LCD), high-quality laminations and conductive textile (35).

The major advantage of PET is its recyclability. PES fibres are the second largest type of fibres produced and consumed worldwide, second only to the cotton fibre.

PES is one of the most common polymers used in textile industry as fibers and fabrics because of their required fiber properties such as higher strength, low moisture absorption, and resistance to shrinkage (36).

Textiles can be distinguished from other materials by their flexibility and comfortability. Conductive yarns used for producing knitted-based sensors generally have poor electromechanical properties. One of the reasons is that the existing conductive yarns made of metals or conductive polymers usually exhibit low elasticity (37).

PES are the most used kinds of textiles. It is reported that poly(ethylene terephthalate) (38), cotton (39) , silica fiber (40) , silk (41) nylon, wool (42), para-aramid (43) (Polyether ether ketone (PEEK) (44) , PES (80) were used with conductive polmers to form conductive textiles.

## 2.4 Polymerization Techniques

Scientific papers published on conductive textiles show us that there is mainly 3 methods are directly applied to textile substrate. In situ chemical polymerization (45), vapour phase polymerization (46), and electrospinning (47).

### 2.4.1 In Situ Polymerization

Most studies have been focused on in situ polymerization to produce conductive textile since this method does not require the destruction of the substrate and provides reasonably good conductivity (48,49). In particular, the in situ polymerization involves monomer intercalation followed by polymerization, which can facilitate extraordinarily high coverage and shell strength owing to the chemical polymerization occurred on the surface of core material, instead of a simple dissolution/precipitation physical process (50).

### 2.4.2 Vapour Phase Polymerization

Vapour phase polymerisation (VPP) is a well established technique in which the monomer is introduced to an oxidant-coated substrate in vapour form. Polymerisation then takes place at the oxidant vapour interface. VPP is a technique that could be used to immobilise materials to the modified electrode surface. Also VPP is for conducting polymers such as PPy, PTh and PANi. VPP of conducting polymers and other non-conducting polymers have extensively been investigated.

VPP methods have been used to deposit thin films on flexible substrate such as wood, cotton and conducting surfaces. VPP methods have also been used in fabrication of electronic nose and DNA sensors. VPP methods provide highly ordered polymer network structure and the polymer thin films remain stable in ambient condition. The growth of thin films at nano-level thickness, high conductivity and surface structure of high integrity provided by VPP can be applied in production of organic optoelectronic devices, antistatic transparent films, plymeric electroluminescent diode and metalisation of insulators (51).

### 2.4.3 Electrospinning

Electrospinning has been known as an efficient technique for the fabrication of polymer nanofibers (78). Various polymers have been successfully electrospun into ultrafine fibers in recent years mostly in solvent solution and some in melt form (52). Electrospinning is currently one of the few techniques that allow the fabrication of continuous fibres with diameters down to a few nanometers. This technique is applicable to virtually every soluble or fusible polymer (53).

Electrospinning is easily realised by applying a high voltage to a capillary filled with the polymer fluid to be spun with help of an electrode. Resulting fibers are collected on a grounded plate, which can be covered with a fabric for example. The process is schematically illustrated in Fig 2.4. (54).

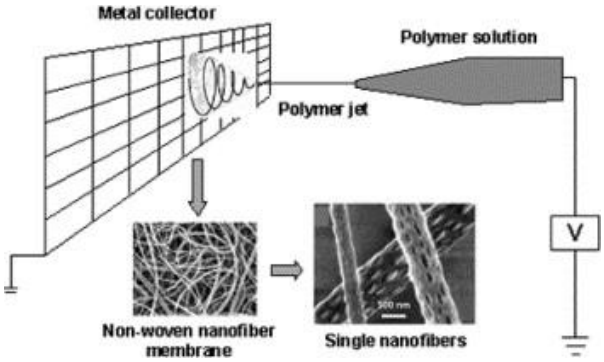
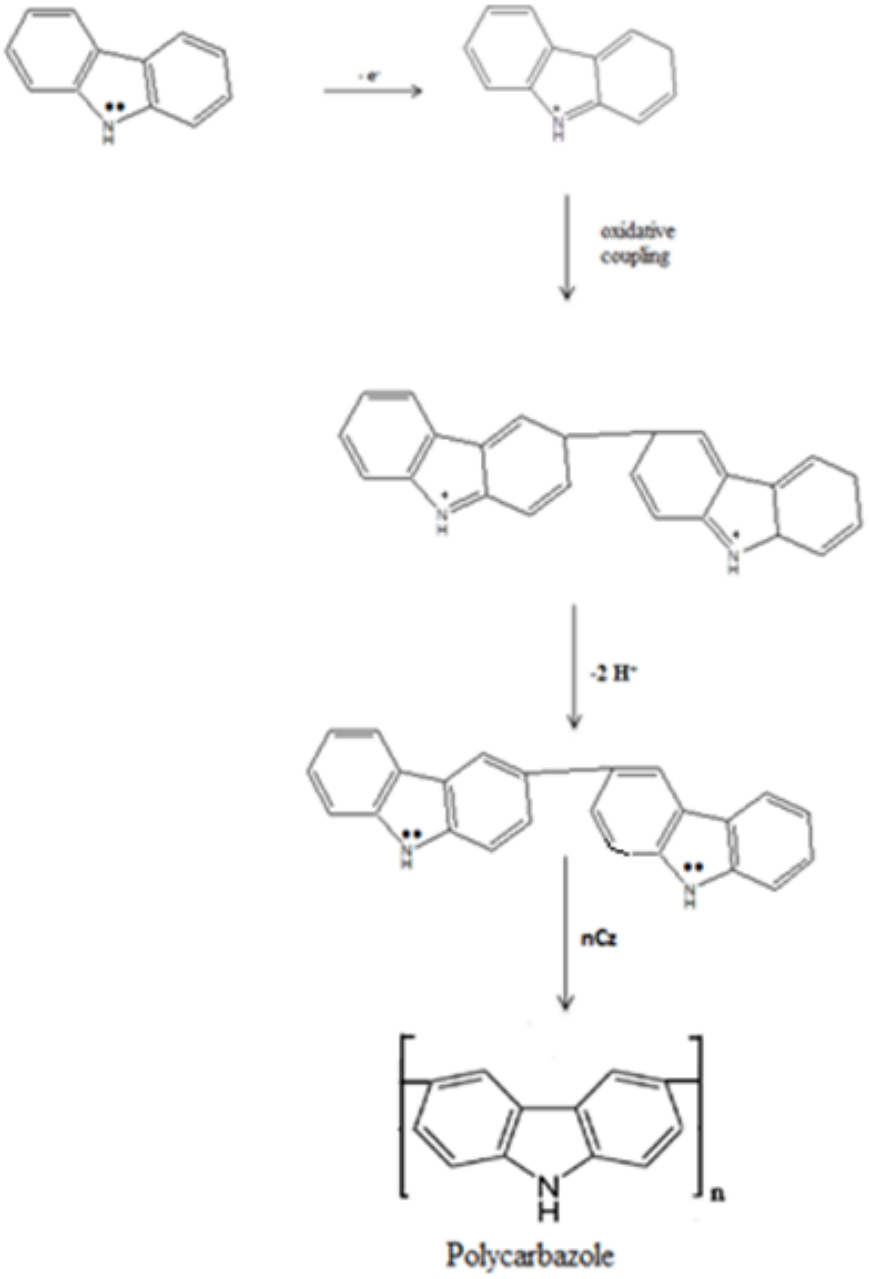



**Figure 2.4:** Schematic form of electrospining.

## 2.5 Polymerization Mechanism of Carbazole

PCz can be formed chemically or electrochemically through oxidative polymerization of Cz. The final form of PCz is that of a long conjugated backbone as seen in figure 2.5. The polymer has resonance structures. In this neutral state the polymer is not conducting and only becomes conducting when it is oxidized. The charge associated with the oxidized state is typically delocalised over several Cz units and can form a radical cation (polaron) or a dication (bipolaron). The physical form of PCz is usually an intractable powder resulting from chemical polymerization and an insoluble film resulting from electropolymerization.

**a) Oxidative coupling**



**b) Free radical**

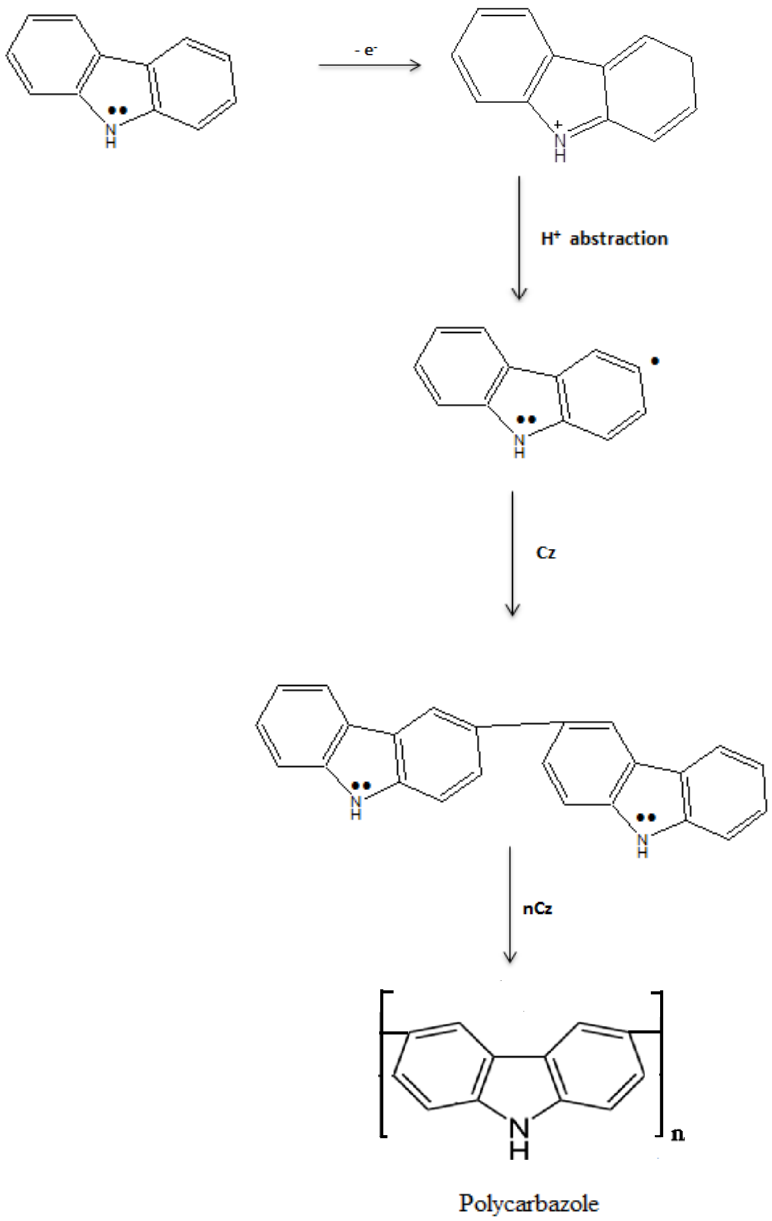



**Figure 2.5:** Polymerization mechanism of PCz. **a-** Oxidative coupling, **b-** Free radical

## 2.6 Electrical Conductivity

Conductivity is the measure of the ease at which an electric charge or heat can pass through a material. A conductor is a material which gives very little resistance to the flow of an electric current or thermal energy. According to electrical properties, materials can be divided into four-types: insulator, semiconductor, conductor and superconductor. In general, a material with a conductivity less than $10^{-7}$ S/cm is regarded as an insulator. A material with conductivity larger than $10^{3}$ S/cm is called as a metal whereas the conductivity of a semiconductor is in range of $10^{-4}$ -10 S/cm depending upon doping degree (56). Figure 2.6 gives information about conductivity of materials.

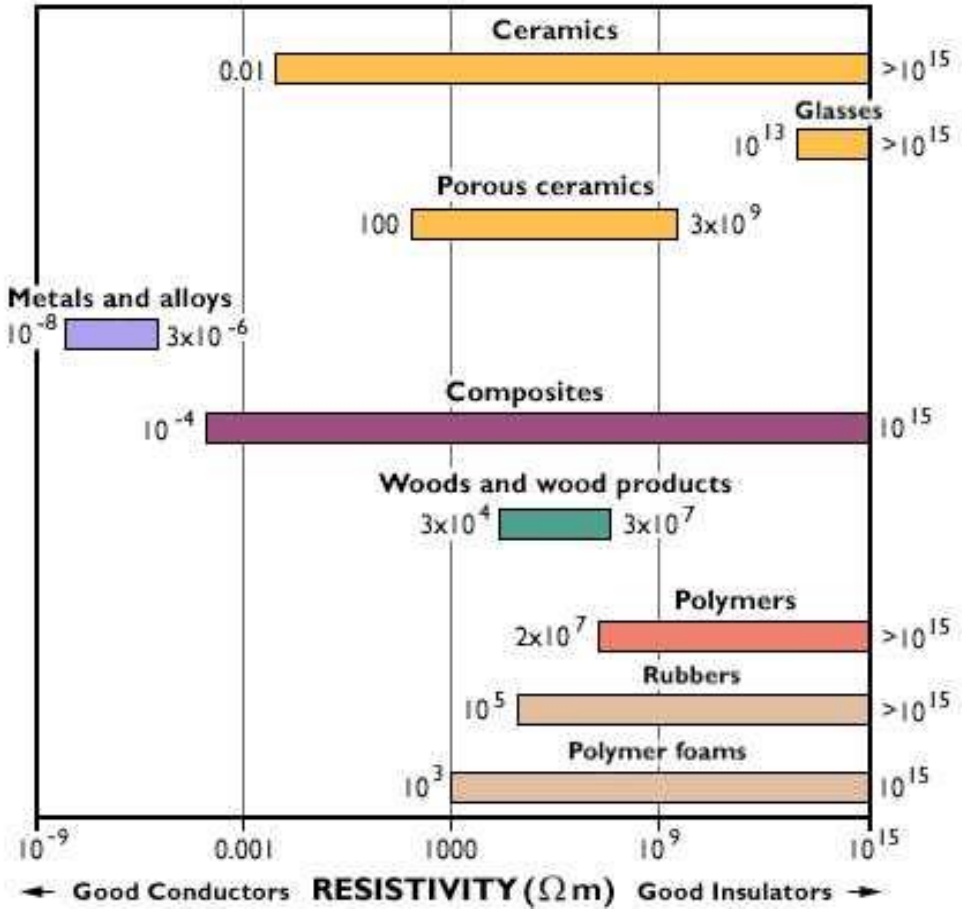



**Figure 2.6:** Conductivity range of some materials.

Ohm's law deals with the relationship between voltage and current in an ideal conductor. This relationship states that: The potential difference (voltage) across an

ideal conductor is proportional to the current through it. The constant of proportionality is called the "resistance", R.

Ohm's Law is given by:

$$V=IxR \quad (2)$$

where V is the potential difference between two points which include a resistance R. I is the current flowing through the resistance.

The electronic properties of any material are determined by its electronic structure. The theory that most reasonably explains electronic structure or materials is band theory. Quantum mechanics stipulates that the electrons of an atom can only have specific or quantized energy levels. However, in lattice of crystal, the electronic energy of individual atoms is altered. When the atoms are closely spaced, the energy levels are form bands. The highest occupied levels constitute the valance band and lowest occupied levels, the conduction band (Figure 2.7).

The electrical properties of conventional materials depend on how the bands are filled. When bands are completely filled or empty no conduction is observed. If the band gap is narrow, at room temperature, thermal excitation of electrons from the valance band to the conduction band gives rise to conducitivty. This is what happens in the case of classical semisonductors. When the band gap is wide, thermal energy at room temperature is unsufficient to excite electrons across the gap and the solid is an insulator. In conductors, there is no band gap since the valance band overlaps the conduction band and hence their high conductivity (57).

Organic polymers usually are described by σ (sigma) bonds and π bonds. The σ bonds are fixed and immobile due to forming the covalent bonds between the carbon atoms. On the other hand, the π electrons in a conjugated polymers are relatively localized, unlike the σ electrons. Plastics are typical organic polymers with saturated macromolecules and are generally used as excellent electrical insulators (58).

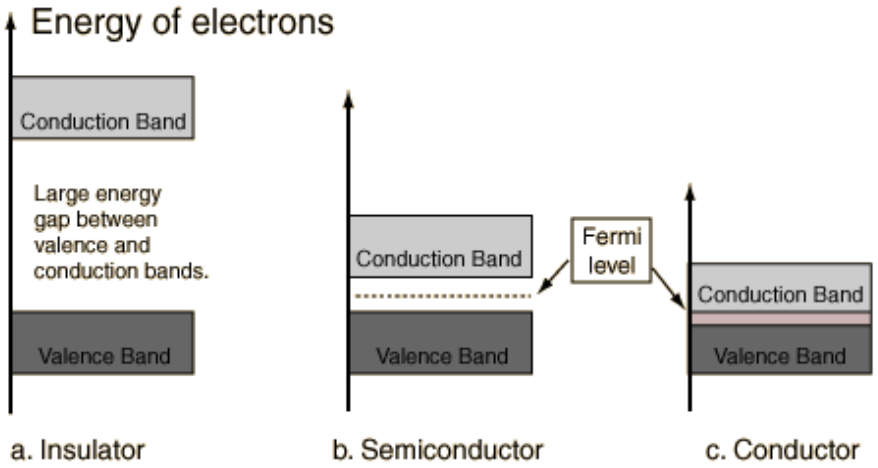



**Figure 2.7 :** Energy band gaps for insulator, semiconductor and conductor.

Charge injection onto conjugated, semiconducting macromolecular chains, denoted as ‘’doping’’, is quite different from doping in conventional inorganic semiconductors such as silicon and germanium.

For semiconducting polymers, doping occurs via oxidation or reduction of the π-electron system for p-type or n-type doping, respectively. Since there can be not uncompensated charge, in semiconducting polymers a counter-ion is inserted into structure.

Doping also serves to (reversibly) shift the electrochemical potential of the polymer, thereby making possible polymer batteries and electrochemically active polymer electrodes, electrochromic phenomena (smart window) and light emitting electrochemical cells.

A four point probe and disc probe are a simple apparatus for measuring the resistivity of semiconductor and conductor samples (Figure 2.8 – A and B). By passing a current through two outer probes and measuring the voltage through the inner probes allows the measurement of the substrate resistivity. Also disc probe gives information about thickness of samples.

| A | B |
| --- | --- |
|  |  |

**Figure 2.8 :** A- Disc probe conductivity measurement device, B- Four probe conductivity measurement device.

## 2.7 Doping mechanism of PCz

The anions released by the oxidant get settled near positive charges to maintain the neutrality of PCz polymeric backbone. The presence of anions (termed generally as dopants) is essential as the charge carriers only move in the vicinity of negative anions. The large surface area of substrate in the reaction bath ensures adsorption of monomer and subsequent growth of polymeric chain on the substrate surface. The polymer growth initiate inside the amorphous region of substrate accompanied by deposition of PCz into substrate (39). It is known that low doping levels give rise to polarons, whereas higher doping levels produce bipolarons. extended oxidation may occur, which may produce bipolarons giving the possibility of the inclusion of more counter ions. This may result in a higher doping level. Figure 2.9 and 2.10 shows polaron and bipolaron of PCz form respectively.

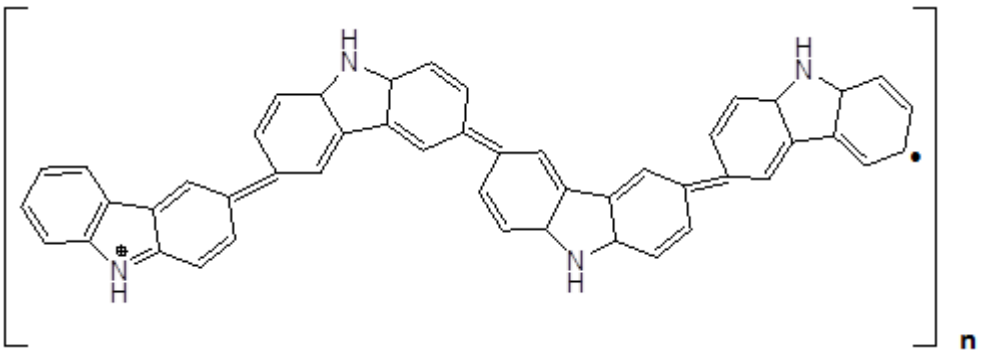


**Figure 2.9:** Polaron form of PCz

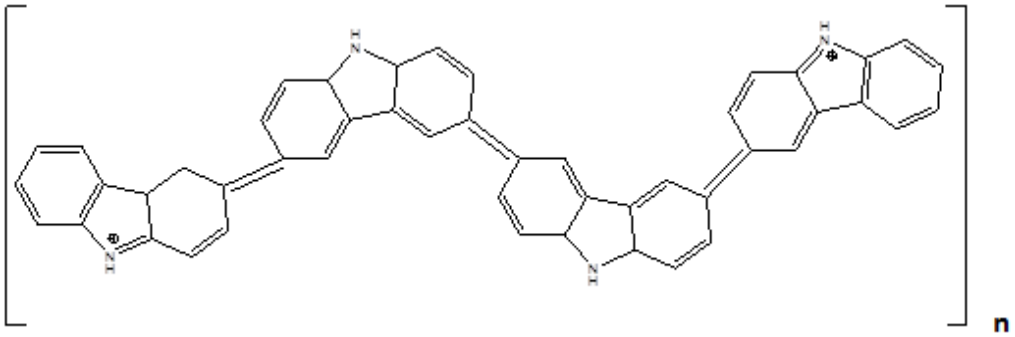


**Figure 2.10 :** Bipolaron form of PCz

Polymerisation takes place via 3 and/or 6 positions of the Cz ring, as these positions are the most reactive. However, polymerisation via the other position is also possible resulting in less conductive form of the polymer (55). Figure 2.11 show these forms of PCz.

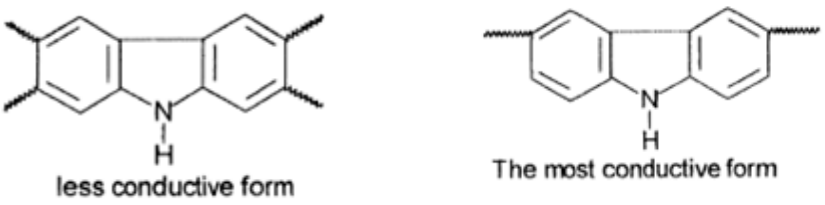



**Figure 2.11 :** Less and most conductive forms of PCz.

## 2.8 Characterization

PES/ PCz composites were characterized by colour analysis, FTIR, SEM, resistivity and DMA measurements.

### 2.8.1 Colour Analysis

Colour analysis can be done with ASTM D6290, E1347, E308 standarts. XYZ model is three dimensional color spaces that allows a precise definition of the color of a test sample. Color analysis can be used to match adjacent parts molded from different materials, or to evaluate color change due to outdoor exposure. Visual color and Spectrophotometer readings can also be affected by surface texture, molding parameters, processing method, and viewing light sources.

Conducting polymers coated onto textile have different colors and colour analysis can be used as one of technique to characterize them. In this study photographes of samples were taken and used for characterization.

### 2.8.2 Resistivity

Resistance of the conductive materials are measured using the disc probe. Because due to the fibrous structure of the textile material, a prop is used consisting of two disks instead of four point probe technique. The electrical properties of conductive textile, depends on the polymer's conductivity. Also disc probe gives information about thickness. The electrical resistance of the conductive textile obtained in this study with the help of two disks is measured with a GWINSTEK LCR meter device.

### 2.8.3 Scanning Electron Microscope (SEM)

The microscopy gives so many details about polymers. In briefly, the sem images the electrons that are reflected from a sample. These images are useful for studying surface morphology or measuring particle size (61) SEM achieves subnanometer resolution in spite of diffraction effects. The SEM consists of a column which houses the filament, electromagnetic lens and beam scanning coils. At the base of the column is the sample chamber that contains the stage and detectors. The SEM

acquires data from the sample one point at a time. At each location where the electron beam impacts the sample, a flux of secondary electrons (SE), backscatter electrons (BSE), X-rays and other signals are emitted from the sample. A portion of each signal travels in a direction such that it enters detector. The detector measures the intensity of electrons emitted at each point on the sample and converts this intensity value into a corresponding 8 bit grayscale value. This digitized value is then displayed on a monitor (62).

### 2.8.4 FT-IR spectrum

Infrared (IR) spectroscopy is a technique based on the vibrations of atoms a molecule. An ir spectrum is commonly obtained by passing ir radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy. The energy at which any peak in absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule (62) Most infrared spectroscopy is carried out by using Fourier-transform infrared (FTIR) spectrometers. This method is based on the interference of radiation between two beams to yield an interferogram, i.e. a signal produced as a function of the change of path length between the two beams. The two domains of distance and frequency are interconvertible by the mathematical method of Fourier transformation. The radiation emerging from the source is passed through an interferometer to the sample before reaching a detector. Upon amplification of the signal, in which high-frequency contributions have been eliminated by a filter, the data are converted to a digital form by using an analog-to-digital converter and then transferred to the computer for Fourier transformation to take place (63).

### 2.7.5 Dynamical Mechanical Analysis (DMA)

Dynamical Mechanical Analysis (DMA) is a method which determines the elastic modulus of a material and its mechanical damping or energy dissipation characteristics as a function of frequency and temperature (63).

The applied force is called stress and is denoted by Greek letter, σ. When subjected to stress, a material will exhibit a deformation or strain, ε. These data have

traditonally been obtained from mechanical tensile testing at a fixed temperature. The slope of line gives the relationship of stress to strain and is a measure of material's stiffness, the modulus. The modulus is dependent on the temperature and the applied stress. The modulus indicates how well a material will work in specific application in the real world. For example, if a polymer is heated so that it passes through its glass transition and changes from glassy to rubbery, the modulus will often drop several decades. This drop in stiffness can lead to serial problems if it occurs at a temperature different from expected. Also DMA gives information about young' modulus. Young's modulus, viscosity (64).

## 3. EXPERIMENTAL

### 3.1 Materials

In this study, Cz was used as monomer. Acetonitrile (ACN), toluene and water were used as solvent. $FeCl_3$ and CAN were used as oxidant. Dodecylbenzene sulfonic acid (DBSA) and *p*-Toluenesulfonic acid (PTSA) were used as wetting agents.

PES used in the study is 100% PES fabric with 0.25 mm thickness. Cz and DBSA, $Na_2CO_3$, Sigma Aldrich, $FeCl_3$, DBSA, PTSA and ACN that are used are Carlo Erba , CAN is from ABCR GmbH & Co.

### 3.2 Polymerization Procedure

Chemical synthesis of PCz is carried out using $FeCl_3$ and CAN as an oxidizing agent. The synthesized polymer follows the reaction pathway as shown in Figure 3.1.

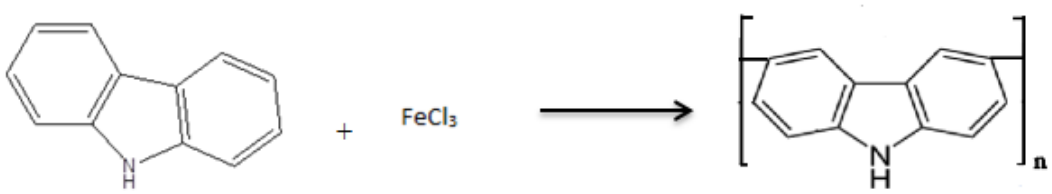



**Figure 3.1** : Reaction of Cz with $FeCl_3$

Optimum conditions which can be seen at Table 3.1 was determined for the polymerization of Cz onto PES.

According to the literature mentioned, there were many choices of solvents which give the good results for conductivity for the synthesis of PCz: THF (67), DMF (68) and ACN (69).

In literature, the effects of noncationic, nonanionic and nonionic surfactants were investigated while obtaining the conductive textile, conductive polymers in the presence of surfactants, were observed to contribute to the uniform coating of the textile surface (59-60).

Therefore, DBSA was used as a surfactant during this study and the effective concentration was determined as 0.02 M. Before the polymerization, in order to purge the oil, that came from the production, and soils and on the textile, firsly it was waited in 2L aqueous solution consisting of 2g of detergent and 2g of $Na_2CO_3$ at 70°C for 30 min, then at 110 °C for 45 min. The optimum conditions for the coating Cz polymer in the form of film on the PES was determined through experimental studies. Optimum conditions are summarized in Table 3.1.

**Table 3.1:** Content which provides optimal conditions for the solution used to wet the PES textile (I, II) and the polymerization reaction (III, IV).

| **Solution** | **I** | **II** | **III** | **IV** |
|---|---|---|---|---|
| Content | 0.02M DBSA<br>15 ml water | 0.02M DBSA<br>15 ml CAN | 0.01 M Cz<br>15 ml ACN | 0.6 M $FeCI_3$<br>0.02 M DBSA<br>15 ml CAN |

Firstly in order to absorb monomers better, a certain weighted PES textile was waited in the aqueous solution I and then waited in the ACN solution II separately, both for 30 min. The PES fabric soaked in this method, was waited in the ACN solution III, where Cz has the same concentration, for an hour in order to ensure that the textile surface is absorbing the monomers. In the next step, to make the polymerization of the monomers absorbed on the PES textile was waited in ACN solution IV, containing DBSA and $FeCl_3$, for 10 min. Instead of polymerization of the monomers in solution, to give opportunity of a slower polymerization, the PES textile was waited in solution III and solution IV with 10 min intervals. The brown colored textile, after 8 repeats, was washed with ACN and the monomers and the oxidizer were taken away from the textile, resulting in the ending of the reaction, and a glass was put on top of the textile in order to prevent it from getting dirty, it was kept

under standard conditions until it was dryed, 16 hours, and then It was weighted and yield calculation was made. The yield is the percentage of the PCz polymer coated onto PES and it is calculated from the difference of the weights of raw PES and coated PES.

The Yield was calculated as follows:

$$\%\, Yield = \frac{Wf - Wi}{Wi} \times 100 \quad (1)$$

where *W*i and *W*f are the initial and final weight, respectively. In this equation, $w_0$ is the weight of the raw textile and w is the weight of the PES/PCz composite after the polymerization.

## 4. RESULTS AND DISCUSSION

PES textile is an insulator, so when it is coated with a conductive polymer, it is expected that its surface resistivity to decrease. The study at comprised of the 3 following steps;

**1-** The synthesis of PCz onto the textile with different concentrations of Cz and also with different concentrations of $FeCI_3$, the surface resistivity of PES/PCz composite which is made on PES surface were measured and yield calculations were made and summarized in Table 4.1.

**2-** Conductivity and capacitance values were measured. To see the evaluation better, the resistivity values were plotted with the change of concentration of $FeCI_3$ (Figure 4.1) and the change of the Cz mole ratio (Figure 4.2 and Figure 4.3).

**3-** Characterization of coated textiles (SEM, Elemental analysis, FTIR, DSC, DMA, colour analysis).

During the polymerization, effect of different parameters such as monomer, oxidant concentration, solvent and polymerization time were investigated in this section.

### 4.1 The effect of $FeCl_3$ and CAN concentrations on the resistivity of PES/PCz composite

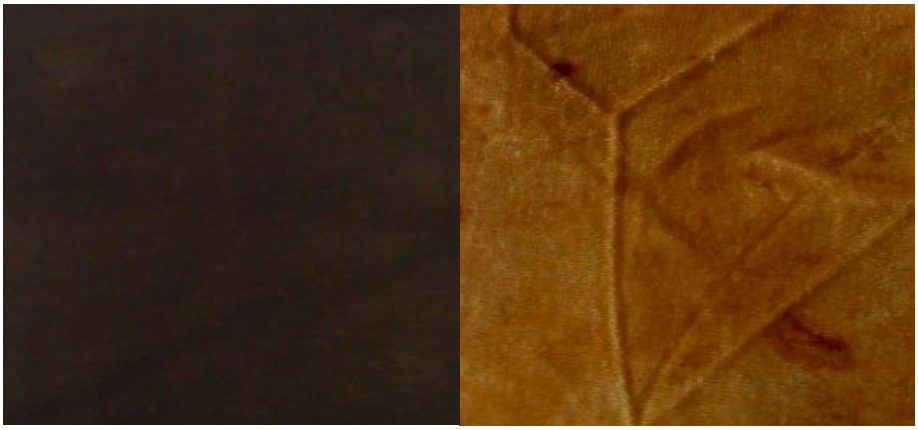
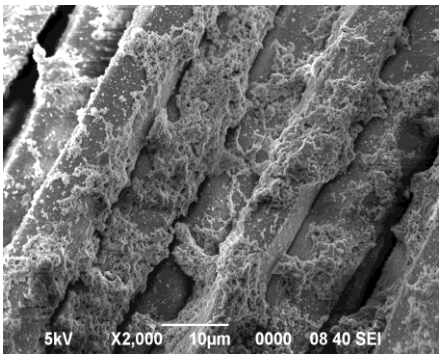
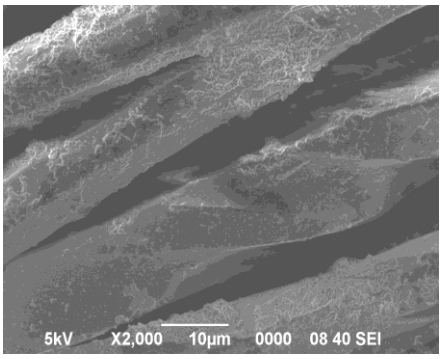
The chloride ($Cl^-$) ions released by the oxidant act as doping agents for doped form of PCz. After analyzing the resistance behavior of $Cl^-$ doped PCz, it was decided to study the effect of $FeCl_3$ as dopants on PCz coated textile.

The amount of oxidant was determined experimentally. Using higher amount oxidant provide to crosslink (70). By the way, the resistance increases. On the other hand, using less oxidant cause to less coating on to textile.

In the first experiments, in situ polymerization rate is too fast in the presence of CAN as oxidant for synthesis of PCz, the polymerization was carried out in the solution

and the Cz monomers could not be able to polymerized on to substrate. The colour change and the difference of SEM images in both cases can be seen at Table 4.1).

**Table 4.1:** Comparison of colour and SEM images of PES/PCz composites obtained by $FeCl_3$ and CAN

| **Experiment no** | **8** | **2** |
|---|---|---|
| **Oxidant** | $FeCl_3$ | CAN |
| **Picture** |  | |
| **SEM** |   |   |

As it can be seen from the Table 4.1, PCz can't penetrate into the textile in presence of CAN. The polymerisation was occured downside of the beaker and PCz can't be able to accumulate onto textile since CAN has high oxidation potential. But the polymerization on the substrate has to be carried out. So $FeCl_3$ was selected as a oxidant.

It is observed that when the $FeCl_3$ concentration increases, the resistance of PES/PCz

composite decreases (Figure 4.1). This behaviour can be explained by creating a PCz layer on PES surface to decrease its surface resistance. After 0,6 M $FeCl_3$ concentration, the side reactions occurring because of the excess $FeCl_3$, like the occurrence of carbonyl on the Cz rings that disrrupt the conjugation of the polymer chain or excessive oxidation which makes the chains crosslinking that results in the decrease of conductivity (70) therefore the resisivity increases. As seen in the Figure 4.2, the resistances of the PES/PCz composites were firstly decreased with the increase in PCz concentration, when the molarity of Cz is more than 0.01, it started to increase.

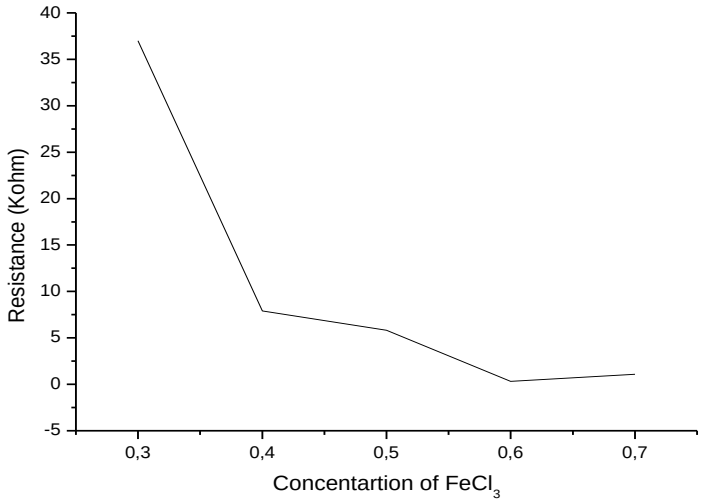



**Figure 4.1:** The resistivity values of PES/PCz composites with different $FeCl_3$ concentrations.

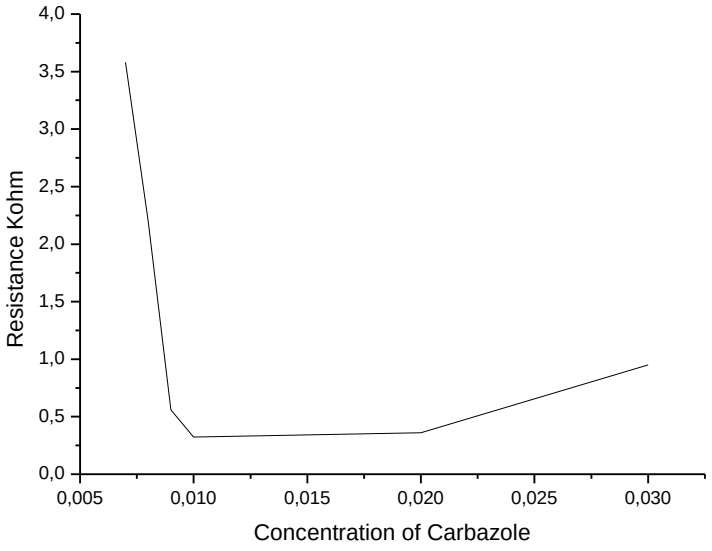



**Figure 4.2:** The resistivity values of PES/PCz composites with different Cz concentrations.

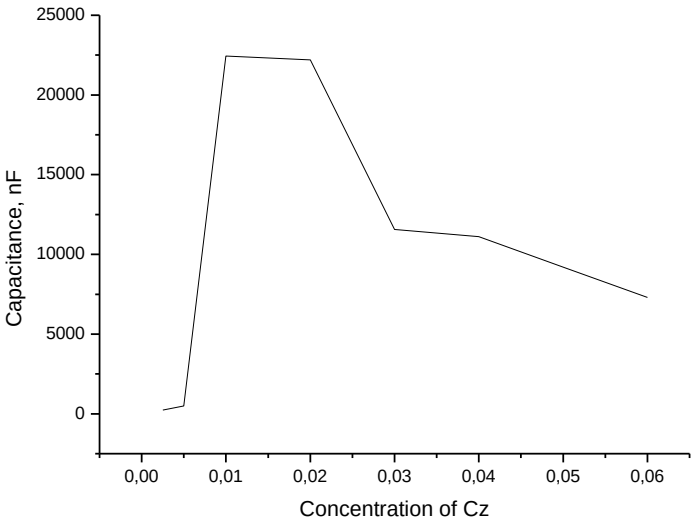



**Figure 4.3:** The capacitance values of PES/PCz with different Cz concentrations.

Figure 4.3 gives information about that capacitance value of PES/ PCz changes with concentration of Cz. PES/ PCz composite obtained with the experiment 8 has the highest conductivity and capacitance values.

**Table 4.2:** The % yield resistivies and capacitance of the PES/PCz composites with changing the Cz and $FeCl_3$ concentrations.

| **Expertiment no** | **Cz mol/L** | **$FeCl_3$ mol/L** | **Yield %** | **Resistivity KΩ** | **Capacitance nF** |
|---|---|---|---|---|---|
| 8 | 0,01 | 0,60 | 4,64 | 0,32 | 22440,00 |
| 9 | 0,02 | 0,60 | 8,08 | 0,36 | 22195,60 |
| 10 | 0,03 | 0,60 | 8,08 | 0,95 | 11566,30 |
| 11 | 0,04 | 0,60 | 8,78 | 0,86 | 11105,40 |
| 12 | 0,005 | 0,60 | 0,20 | 19,81 | 492,60 |
| 13 | 0,0025 | 0,60 | 0,40 | 68,50 | 233,80 |
| 14 | 0,009 | 0,60 | 2,22 | 0,56 | 8293,00 |
| 15 | 0,008 | 0,60 | 1,75 | 2,20 | 4437,30 |
| 16 | 0,007 | 0,60 | 1,42 | 3,58 | 3558,70 |
| 17 | 0,05 | 0,60 | 9,46 | 0,75 | 9198,50 |
| 18 | 0,06 | 0,60 | 7,14 | 0,91 | 7306,30 |
| 19 | 0,01 | 0,70 | 2,54 | 1,09 | 5821,70 |
| 20 | 0,01 | 0,50 | 1,44 | 5,81 | 1523,70 |
| 21 | 0,01 | 0,40 | 2,10 | 7,96 | 1334,00 |

| | | | | | |
|---|---|---|---|---|---|
| 22 | 0,01 | 0,30 | 1,50 | 0,25 | 185,90 |
| 23 | 0,01 | 0,20 | 1,90 | 37,14 | 23,16 |
| 24 | 0,01 | 0,10 | 0.30 | 189,00 | 0,44 |

Table 4.2 reports the relationship between the electrical surface resistivity and the capacitance values of PES/PCz composites with the yield values of the experiments performed by varying monomer and oxidant concentrations. As seen from the Table 4.2 the surface resistivity of PES/PCz was drastically balanced as a result of concentration of PCz and $FeCl_3$.

The stability of PCz coated textiles is given at Table 4.3. As it can be seen, the resistance values increase gradually by time. The atmospheric oxidation causes chemical degradation of PCz by disrupting the continuity in conjugation length and subsequently hinders the charge movement as well as charge hopping at defect sites. The reaction of oxygen on PCz backbone leads to formation of a, b-unsaturated carbonyl groups which are believed to act as an electron trap (39).

**Table 4.3:** Stabilities of PES/PCz composites.

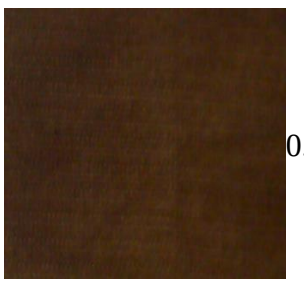
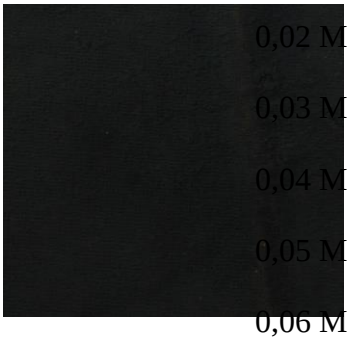
| **Experiment no** | **[Cz]** | **Resistance 1 (Kohm)** | **Resistance 2 (Kohm)** | **Resistance 3 (Kohm)** |
|---|---|---|---|---|
| 8 | 0,01 | 0,322 | 1,444 | 25,70 |
| 9 | 0,02 | 0,360 | 0,85 | 21,24 |
| 10 | 0,03 | 0,950 | 1,88 | 19,00 |
| 11 | 0,04 | 0,860 | 2,02 | 16,42 |
| 12 | 0,005 | 19,81 | 609 | 1581 |

| | | | | |
|---|---|---|---|---|
| 13 | 0,0025 | 68,50 | 516,8 | 871,90 |
| 14 | 0,009 | 0,56 | 2,29 | 41,22 |
| 15 | 0,008 | 2,20 | 6,84 | 310,20 |
| 16 | 0,007 | 3,58 | 19,6 | 377,10 |
| 17 | 0,05 | 0,75 | 1,31 | 11,09 |
| 18 | 0,06 | 0,91 | 1,55 | 12,27 |
| 19 | 0,01 | 1,09 | 4,56 | 48,94 |
| 20 | 0,01 | 5,81 | 23,13 | 1496 |
| 21 | 0,01 | 7,96 | 244.6 | 229.8 |
| 22 | 0,01 | 0,259 | 1611 | 1799 |
| 23 | 0,01 | 37,14 | 2222.3 | 2061.30 |
| 24 | 0,01 | 1921 | 658.7 | 709 |

### 4.2 The effect of Cz concentration on the colour of PES/PCz composite

The PES/PCz composite obtained with experiment 8 which has the most conductivity is dark brown, while experiment 13 has the lowest conductivity is light brown. This lower conductivity is due to the low thickness of coatings. Colors of (9-11,17,18) almost the same. When the color gets dark brown, conductivity increases. But for more than 0,01 M Cz (experiment 8), it shows vice versa. It means that resistance increases. Brown color change to dark green. Pictures of PES/PCz composites is given at Table 4.4.

**Table 4.4:** Color contrast of PCz coated textiles changing with concentration of Cz.

| Experiment | Sample | [Cz] | Experiment | Sample | [Cz] |
|---|---|---|---|---|---|
| Uncoated PES |  | | 15 |  | 0.008 M |
| 13 |  | 0.0025 M | 14 |  | 0.009 M |
| 12 |  | 0.005 M | 8 |  | 0.01 M |
| 16 |  | 0.007 M | 9<br>10<br>11<br>17<br>18 |  | 0,02 M<br>0,03 M<br>0,04 M<br>0,05 M<br>0,06 M |

### 4.3 The effect of wetting agent on the resistivity of PES/PCz composites

Wetting agent was used to improve wetting of PES substrate. DBSA and PTSA was used as wetting agent. The more planer structure of the sulfonic acid dopants was believed to be responsible for improvement in conductivity as it helps in interplanar stacking of dopant molecules. This peculiar positioning of dopants between PCz chains facilitates interchain charge hopping more readily than small dopants such as $Cl^-$ ions. Hence, the increased hopping opportunities contribute toward higher conductivity. Furthermore, the variation in the performance of the individual sulfonic acid dopants can be attributed to the two aspects, molecular size and concentration of dopants. The size of dopant molecules in terms of bulkiness alters the charge transfer in a remarkable way (39 ).

The amount of wetting agent was found experimentally(Table 3.1) and was used as 0,02 M. This amount was accepted as a starting point for determining the necessary concentration of DBSA. When we don't use wetting agent, there is no sufficiently coating. Two step deposition was carried out, the half of this amount of wetting agent was added to the both of 15 ml solutions. Experiments with different wetting agents are given at Table 4.5. The best conductivity value of the PES/PCz composite was obtained in the case of DBSA(experiment 8).

**Table 4.5:** Experiments with different wetting agents.

| **Experiment** | **[Cz]** | **[$FeCl_3$]** | **Solvent** | **Wetting agent for Cz** | **Wetting agent for $FeCl_3$** | **Total time (min.)** | **Resistance Kohm** |
|---|---|---|---|---|---|---|---|
| 3 | 0,01 | 0,6 | ACN | PTSA | PTSA | 180 | 1,92 |
| 7 | 0,01 | 0,6 | ACN | PTSA | DBSA | 165 | 4 |
| 8 | 0.01 | 0.6 | ACN | DBSA | DBSA | 270 | 0.322 |

### 4.4 The effect of solvent on the resistivity of PES/PCz composites

According to literature, toulene (71), ACN, methanol (72), water (73) , ethanol (74) choloroform (75) have been used as solvent to coat a polymer onto films and fabrics.

Toluene, ACN, water were used for the experiments. Changes in resistance with solvents are given at Table 4.6. Toluene was used at the experiments 4 and 5 .The most conductive properties was obtained from ACN (experiment 8). Therefore ACN is accepted as most efficiently.

**Table 4.6:** Changes in resistance of PES/PCz composites with solvents.

| **Deney no** | **[Cz]** | **[$FeCl_3$]** | **Solvent for Cz** | **Solvent for $FeCl_3$** | **Time (min.)** | **Resistance (Kohm)** |
|---|---|---|---|---|---|---|
| 4 | 0,01 | 0,6 | Toluene | Toluene | 270 | 6,26 |
| 5 | 0,01 | 0,6 | Toluene | ACN | 270 | 10,78 |
| 6 | 0,01 | 0,6 | ACN+water | ACN | 270 | No coating |
| 8 | 0.01 | 0.6 | ACN | ACN | 270 | 0.322 |

### 4.5 The effect of polymerization time on the resistivity of PES/PCz composites

Time affects the resistivity of samples resistivity of samples coated for longer polymerization times is lower due to accumulated polymer concentration (76). Changes in resistance with different polymerization time is given at Table 4.7. lnitially, the textile specimen was immersed into Cz for 12 hours to be able to get wet, then it was the immersed into $FeCl_3$ solution for 12 hours again (Experiment 1). But unsufficient polymerization on the textile was obtained in this experiment. Henceforth, the textile specimen was immersed into Cz solution to be able to get for 1 hour, then immersed into $FeCl_3$ solution for 10 min. After that, the sample was immersed into Cz solution for 10 min. It was repeated for 8 times (Experiment 8).

With increasing duration of polymerization from 270 min. to 540 min. , the surface resistivity increased (Formula 28).

**Table 4.7:** Changes in resistance with different polymerization time.

| **Experiment** | **[Cz]** | **[$FeCl_3$]** | **ACN (ml)** | **Waiting time in Cz (min)** | **Total time (min)** | **Resistance (Kohm)** |
|---|---|---|---|---|---|---|
| 1 | 0,01 | 0,7 | 20 | 12 h | 720 | No coating |
| 8 | 0,01 | 0,6 | 30 | 60 min | 270 | 0,322 |
| 27 | 0,01 | 0,6 | 30 | 120 min | 540 | 259 |

### 4.6 SEM results

The SEM picture of PCz powder reported in previous studies (16) was given at Figure 4.4. In the absence of tekstile, PCz was obtained in the solution. When the polymerization is done on PES, instead of the solution, the same granular structure is observed to be accumulated on the textile The SEM images of the PES/PCz composite and uncoated textile were presented in Table 4.8. In different magnification the uncoated textile weave structure is smooth and clear. When it is coated with PCz it is seen that the places between the fibers are partially filled with polymer and when the magnification increases, the existance of the polymer is seen more clear.

**Figure 4.4:** The SEM image of PCz powder

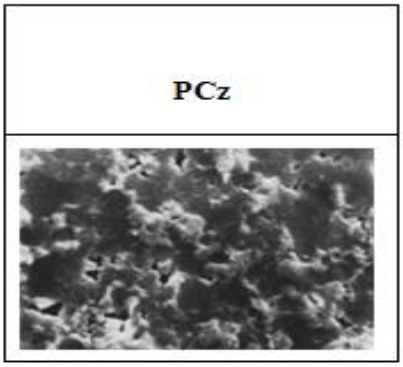
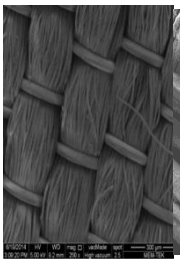
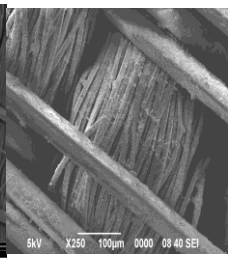
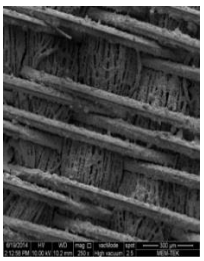
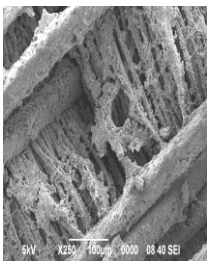
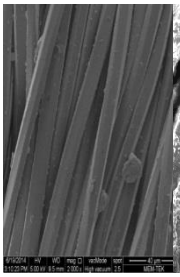
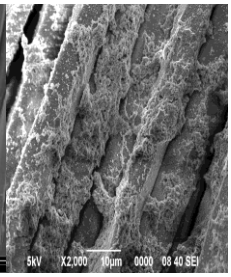
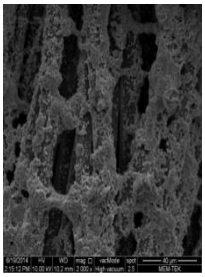
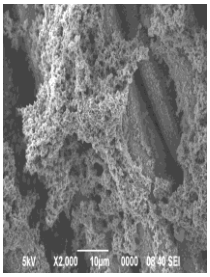
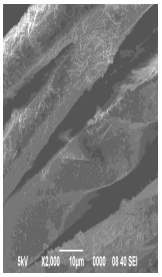
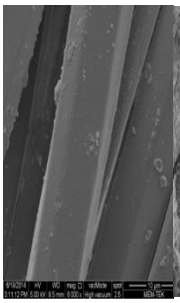
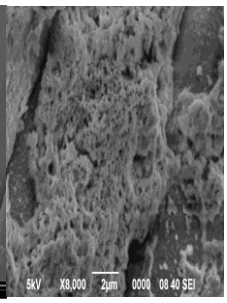
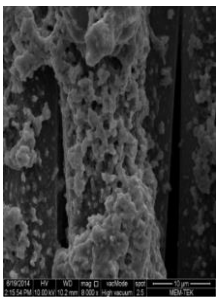
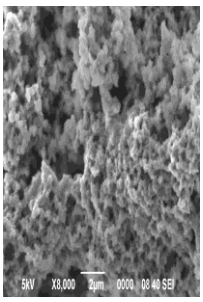
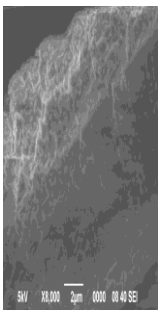
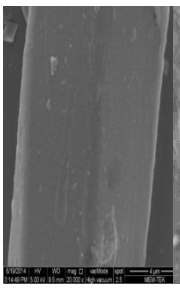
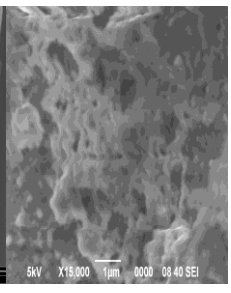
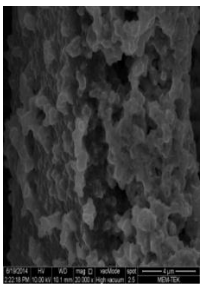
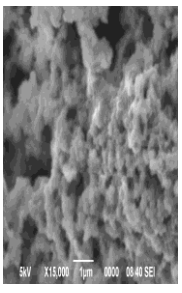
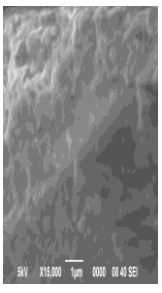


**Table 4.8:** SEM images of PES and PES/PCz composites under different magnification.

| Magnitute | Uncoated PES | Experiment 12 | Experiment 8 | Experiment 21 | Experiment 2 |
|---|---|---|---|---|---|
| **X250** |  |  |  |  |  |
| **X2000** |  |  |  |  |  |
| **X8000** |  |  |  |  |  |
| **X20000** |  |  |  |  |  |

## 4.7 FT-IR Spectrum Results

FT-IR spectra of uncoated PES and PES/PCz composite were given in Figures 4.5, 4.6, 4.7, 4.8, 4.9 and 4.10 respectively. The wavelengths of the peaks and the corresponding vibrations that are obtained from the FT-IR spectrums of PCz given at Table 4.9 At the FT-IR spectrum of PES, it is seen that there are characteristic peaks of -C=O stretching at 1708 cm-1, -C-C stretching at 1240 $cm^{-1}$ ,-C-O-C stretching at 1097 cm-1 and C-H bending at 720 cm-1 (11) (Figure 4.5)

The peak at 871 $cm^{-1}$ belongs to 1,2,4 three substituents benzene, at 1010 $cm^{-1}$ to C-H vibration, at 1095 $cm^{-1}$ to $Cl^-$ acted as dopant ion to neutralize the positively charged polymer chain and to make it a conductive as a dopant (73 at 1407 $cm^{-1}$ to C=N strain, the peak of PCz at 1622 $cm^{-1}$ is the aromatic C=C peak, at 2983 $cm^{-1}$ to C-H strain and at 3360 $cm^{-1}$ to N-H strain are all observed for PES/PCz composite. (Figure 4.6, Figure 4.7)

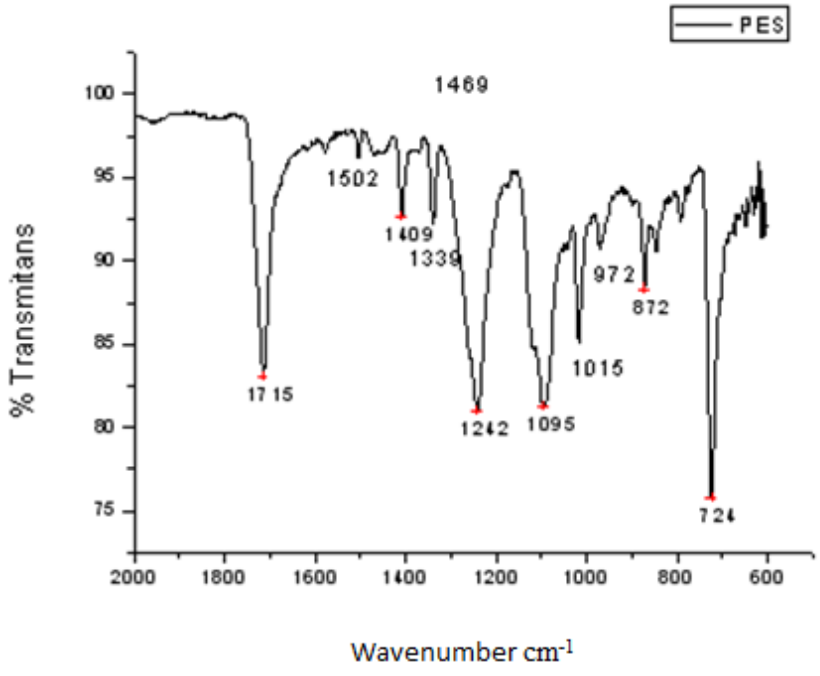



**Figure 4.5:** FT-IR spectrum of uncoated PES.

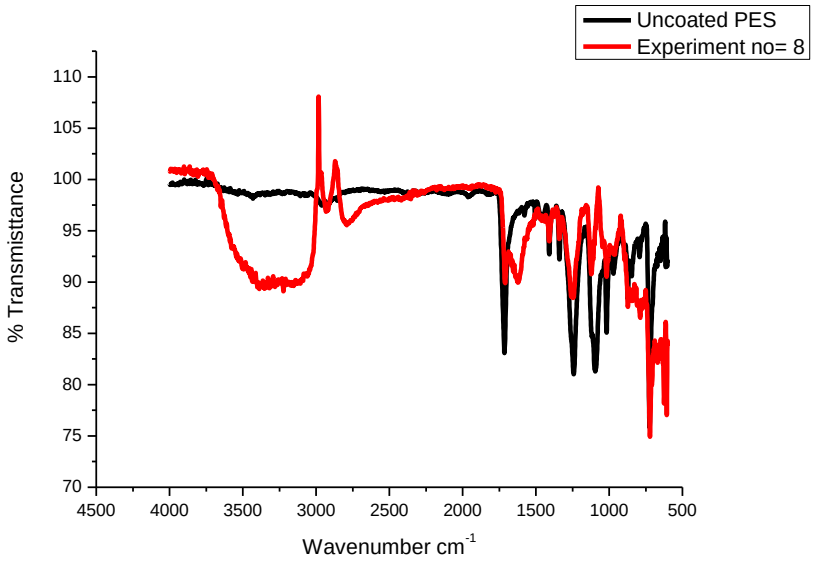



**Figure 4.6:** FT-IR spectrum of PES/PCz composite obtained at experiment 8. [Cz] = 0.01 M

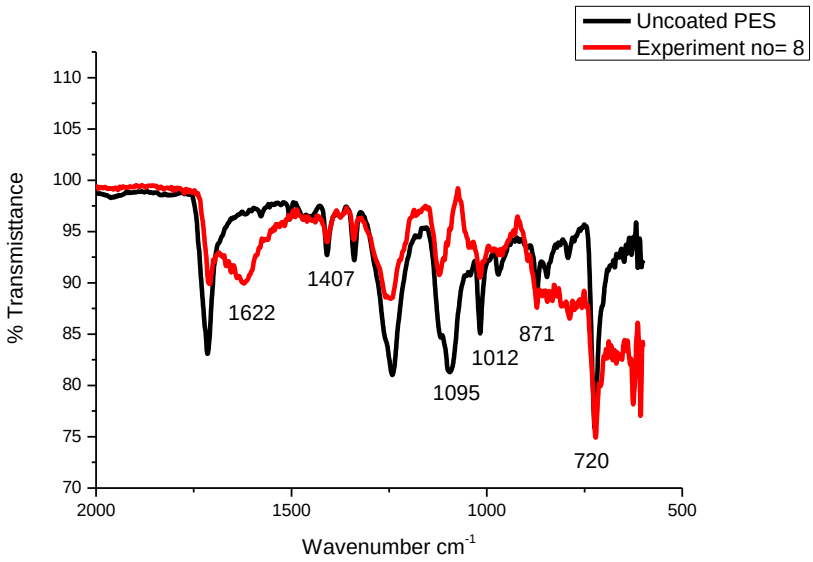



**Figure 4.7:** FT-IR spectrum of PES/PCz composite obtained at experiment 8. [Cz] = 0.01 M.

**Table 4.9:** The wavelenghts and the corresponding vibrations of the peaks of uncoated PES and PES/PCz composites obtained from FT-IR spectra.

| **Wavenumber $cm^{-1}$** | **Corresponding vibrations** |
|---|---|
| 720 | C-H bending |
| 871 | 1,2,4 tree substitute benzene |
| 1012 | C-H vibration |
| 1095 | $Cl^-$ (dopant) |
| 1407 | C=N stretching |
| 1622 | C=C aromatic stretching |
| 2933 | C-H stretching |
| 3360 | N-H stretching |

The FT-IR spectra of the specimens synthesized with the experiments 9,12 and 16 are shown in Figure 4.8, Figure 4.10 , Figure 4.10. Increase in the Cz concentration cause to stronger peaks. The effect can be seen in the Figure 4.8, Figure 4.9, Figure 4.10. Less molar concentration of Cz cause to weak peak at the FT-IR at PES/PCz composites. But higher concentration of Cz shows strong peaks. The difference

intencities at different composites obtained with different Cz concentrations can be explained that increasing thickness of coating material on the PES surface.

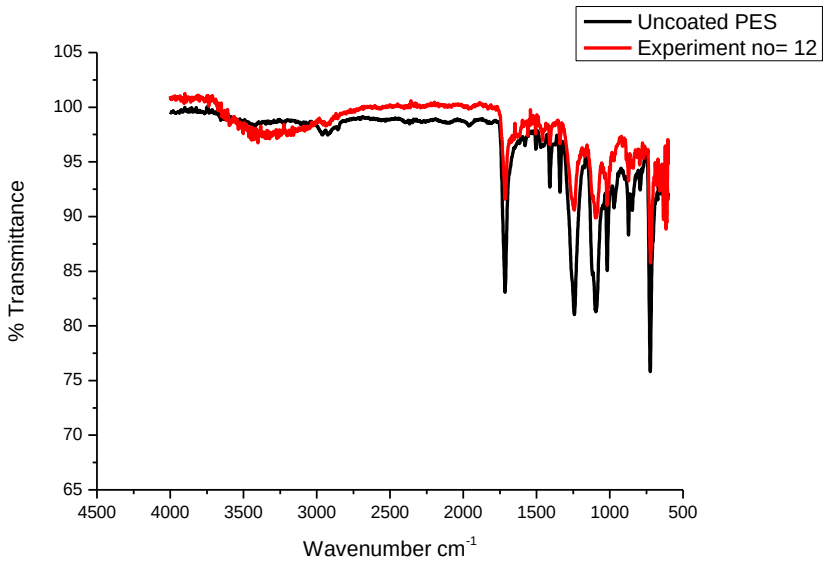



**Figure 4.8:** FT-IR spectrum of PES/PCz composite obtained at experiment 12. [Cz]= 0.005 M

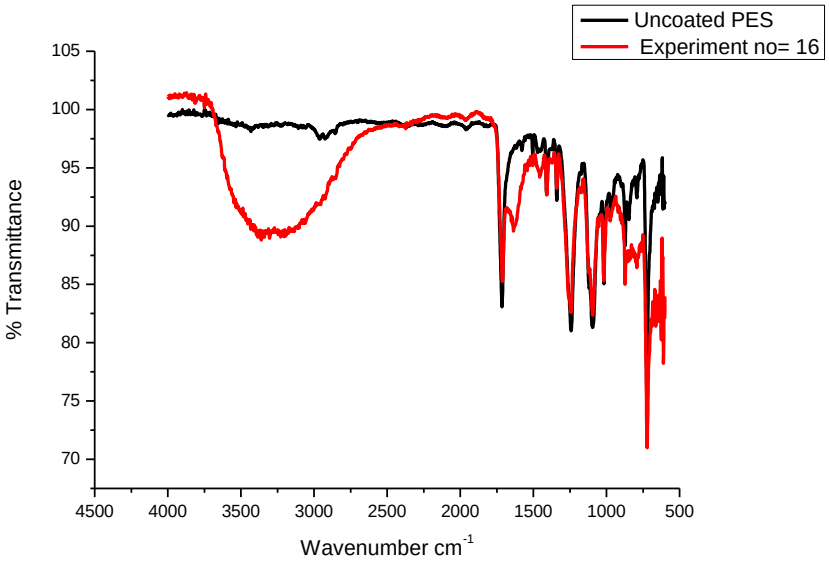



**Figure 4.9:** FT-IR spectrum of PES/PCz composite obtained at experiment 16. [Cz]= 0.007 M.

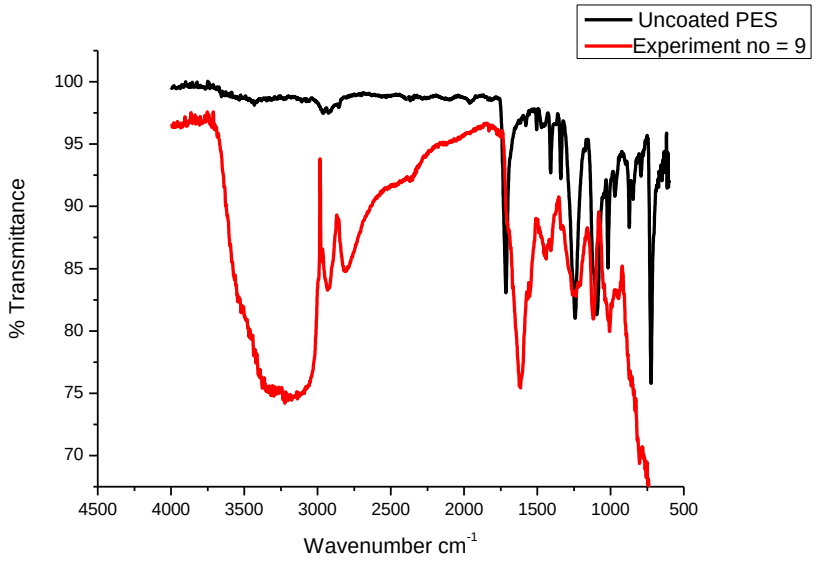



**Figure 4.10:** FT-IR spectrum of PES/PCz composite obtained at experiment 9. [Cz]=0.02 M

### 4.8 DMA measurement results

The DMA measurement results of PES, PES/PCz composites were summarized at Table 4.10. As can be seen, when PES/PCz case, the module gives a little amount of increase considered to PES. A similar effect, in literature, reported as PANI coated polyetilenetereflatat (PET) textile. Tensile module is better than uncoated PET and was explained by filling the blanks on textile with PANI during the coating process (78).

**Table 4.10:** DMA Results of PES and PES/PCz composite.

| Polymer | Young Module (MPa) |
|---|---|
| PES | 431 |
| PES/PCz | 467 |

## 5. CONCLUSION

Cz was polymerized with $FeCl_3$ by chemical method on to PES surface and PES/PCz composites were obtained. The oxidant, solvent, polymerization time and wetting agent effects were investigated.

The efficiency of CAN was so hıgh for to accumulate polymer onto textile substrate instead of the polymerization in solution. In the case of $FeCl_3$ which has lower oksidation potential than CAN, PCz could be coated on textile substrate with good electrical conductivity. Therefore $FeCl_3$ was decided to use as oxidant for polymerization of Cz onto PES surface.

Solvent effect was investigated by using toluene, ACN and water. In the case of ACN, the highest conductivity were obtained.

Wetting agent affect was also investigated. DBSA and PTSA were used as wetting agent. The highest conductivity was obtained with DBSA.

At DMA measurements, uncoated PES and PES/ PCz composites have similar mechanical behavior. But in the case of PES/ PCz, young module is higher than PES.

At FT-IR results, PES and PCz/PES composite shows characteristics peaks and 1095 $cm^{-1}$ corresponding to doping anion ($Cl^-$) has been observed.

Increasing in the Cz concentration caused to increasing amount of polymer on PES. The stronger peaks at FT-IR spectra and the smoother surface at SEM images support the same idea. The tensile module of PES/PCz composites was better than uncoated PES and can be explained by filling the blanks on textile with PCz during the coating process.

The lowest resistivity value was measured as 0.32 Ω for PES/PCz composites when Cz concentration was 0.01 M.

As a result, with the advantages of good mechanical property of PES and conductivity property of PCz, PES/ PCz composite demonstrates that it is favorable

for conductive textile applications such as sensor, antenna, military and sports applications.

## 6. REFERENCES


1- **SAÇAK, M**. Bölüm 1. Polimer Kimyasına Giriş. Ankara: s.n., (1998), s. 1.

2- **Nalwa H.S. (Ed.),** Handbook of organic conductive molecules and polymer, John Wiley, New York, 1997

3- **Skotheim T.A.,Reynolds J.R.** CRC Press, Taylor & Francis Group, (2007), Handbook of Conducting Polymers, Conjugated Polymers, Third Edition.).

4- "The Nobel Prize in Chemistry (2000) - Advanced Information". Nobelprize.org. Nobel Media AB 2014. Web. 15 Jan 2015.

5- **V. Raj, D. Madheswari, M. Mubarak Ali**, Chemical Formation, Characterization and Properties of Polycarbazole, Journal of Applied Polymer Science, Vol. 116, 147–154 (2010)).

6- **N. Muthukumar, G. Thilagavathi,** Development and chracaterization of electrically conductive polyaniline coated fabrics, Indian journal of chemical technology, vol. 19, November 2012, pp. 434-441.

7- **Dipayan Das, Kushal Sen, Aditya Saraogi, Syamal Maity**, Experimental Studies on Electro-Conductive Fabric Prepared by In Situ Polymerization of Thiophene

onto Polyester, Journal ofAppliedPolymer Science,Vol. 116, 3555–3561, 2010.

8- **Saraç, A.S., Ustamehmetoglu, B., Erbil,C. and Uzelli,G,** (1995), J. Polym. Sci. Part A: Polym. Chem., 33, 1581-1587.).

9- **Z. Yıldız, I. Usta, A. Gungor,** (2013), Fibers & Textiles, s 32-37. Y. Li, X.Y. Cheng, M.Y. Leung, J. Tsang, X.M. Tao, M.C.W. Yuen, (2005), Synthetic Metals 155. S 89-94. Derrick, T, Kathirgamanathan, P, Toohey, MJ, Chubb, JN. (1999), Electrostatics, vol. 163, s 313-319.) PTh and its substutients.

10- **Das D, Sen K., Saraogi A. and Maity S.,** (2010), J. Of Applied Polym. Sci, 1163555-3561.

11- **Bashir T., Skrifvars M. and Persson N.K.,** (2012), Polymer Adv. Tech. 23, 611-617.

12- **Schweizer F. J, Schawaller M, Buchmeiser D.**, Macromol MR., (2012),Mater. & Eng., 297,2, 123-127.

13- **A.S. Sarac, O.Yavuz, E. Sezer**, Electrosynthesis and study of carbazole–acrylamide copolymer electrodes, Polymer 41 (2000) 839–847).

14- **Bashir T., Skrifvars M. and N.K,** (2011), Persson Mater. Tec 26, 3 135-139. Mokhtari, J. (2012), Nouri M, Fibers &Polm. 13, 2, 139-144.)

15- **Kim B., Koncar V.,. Dufour C,** (2006), Journal of Applied Polymer Science, Vol. 101, 1252–1256. Oh K.W., Hong K.H., Kim S. H., (1999), J. Of Appl. Polym. Sci, 74, 2094-2101.

16- **Saraç A.S., Sezer E., and Ustamehmetoglu B.** (1997), Polym. Adv. Tech., 8, 556-562

17- **Jean-louis HALARY, Françoise LAUPRETRE, Lucien MONNEREIE**, Polymer Materials Macroscopic Properties and Molecular Interpretations,WILEY,2011- itu kütüphane

18- **ODIAN, George.** Principles of polymerization. 4rd ed. College of Staten Island City University of New York, 2004.

19- **J .A. Chilton.** Special Polymers for Electronics and optoelectronics, Principal Scientist, GEC-Marconi Materials Technology Ltd, Caswell, UK, 1995

20- **Gordon G. Wallace, Geoffrey M. Spinks, Leon A.P. Kane-Maguire, Peter R. Teasdale,** Conductive Electroactive Polymers, Second Edition, CRC Press, 2002.

21- Bhavana Gupta, Rajiv Prakash, Ambrose Melvin, Chemical Synthesis of Polycarbazole (PCz), Modification and pH Sensor Application, 2012 Sixth International Conference on Sensing Technology (ICST) )

22- **Teasdale, P.R.; Wallace, G.G. Chimi Oggi.** 1992, 10: 19.

23- **Riley, P.J.; Wallace, G.G. J. Int. Mat. Syst. Struct.** 1991, 2: 228.

24- **Wallace, G.G.** Mat. Forum 1992, 16: 111.

25- **Talaie, A.; Sadik, O.; Wallace, G.G.** J. Mat. Syst. Struct. 1993, 4: 123.

26- **Mirmohseni, R.; Price,** W.E.; Wallace, G.G.; Zhao, H. J. Int. Mat. Syst. Struct. 1993, 4:43.

27- **Mohammad Soleimani, Mohsen Ghorbani, Hossein Eisazadeh**,

Conductive Polymer-Biosorbent Nanocomposite. Lambert Academic Publications.2012).

28- **Graebe and Glaser**, Ber.,5,12(1872);Ann., 163,343(1872). – Compare Ziedler, Ann., 191,296(1878))

29- **Sanda, F.; Nakai, T.; Kobayashi, N.; Masuda, K. Macromolecules** 2004, 37, 2703–2708. 25- Mello, S. V.; Dynarowicz-Łe˛tka, P.; Dhanabalan, A.; Bianchi, R. F.; Onmori, R.; Janssen, R. A. J.; Oliveira, O. N., Jr. Colloid. Surf. A 2002, 198–200, 45–51.

30- **Mello, S. V.; Dynarowicz-Łetka, P.; Dhanabalan, A.; Bianchi, R. F.; Onmori, R.; Janssen, R. A. J.; Oliveira, O. N., Jr. Colloid. Surf. A** 2002, 198–200, 45–51.).

31- **Nordin, NH, Ramli, MR, Othman, N, Ahmad, Z,** Synthesis of carbazole-substituted poly(dimethylsiloxane) and its improved refractive index, (2015), JOURNAL OF APPLIED POLYMER SCIENCE, Volume: 132.,

32- **Rui-ping Qin, Yu-rong Jiang, Hao-xing Zhang, Kai-xuan Zhang, Qun-ying Zhang and Fang-gao Chang,** Fine-tuning of Polymer Photovoltaic Properties by the Length of Alkyl Side Chains, Chinese Journal of Polymer Science Vol. 33, No. 3, (2015), 490–498.

33- **Dahai Peng · Wei Zhang · Guipeng Tang · Jun Zhou · Jiaomei Hu · Qiufang Xie · Chaofan Zhong,** Novel dye sensitizers of main chain polymeric metal complexes based on complexes of 2-(2′-pyridyl)benzimidazole derivative with Zn(II), Co(II): synthesis, characterization, and photovoltaic performance for dye-sensitized solar cells, J IRAN CHEM SOC (2015) 12:397–404) ).

34- **Bhavana Gupta, Rajiv Prakash, Ambrose Melvin,** Chemical Synthesis of Polycarbazole (PCz), Modification and pH Sensor Application, 2012 Sixth International Conference on Sensing Technology (ICST)

35- **Tariq Bashira, Mikael Skrifvarsa and Nils-Krister Persson**- Synthesis of high performance, conductive PEDOT-coated polyester yarns by OCVD technique, Polym. Adv. Technol. 2012, 23 611–617).

36- **B.L. Deopura1, N.V. Padak**- SYNTHETIC TEXTILE FIBRES: POLYAMIDE, POLYESTER AND ARAMID FIBRES, Chapter 5, 2015.

37- **Li Guo, Lena Berglin and Heikki Mattila**. Improvement of electro-mechanical properties of strain sensors made of elastic-conductive hybrid

yarns, Textile Research Journal 82(19) 1937–1947)..

38- **Pen-Cheng Wang, Jing-Yu Yu, Kuan-Hsun Li**, All-organic polymer-dispersed liquid crystal light-valves integrated with electroactive anthraquinone-2-sulfonate-doped polypyrrole thin films as driving electrodes, Materials Chemistry and Physics 130 (2011) 1346– 1350.).

39- **Amol J. Patil, Smita C. Deogaonkar,** Conductivity and Atmospheric Aging Studies of Polypyrrole-Coated Cotton Fabrics, Journal of Applied Polymer Science, Vol. 125, 844–851 (2012) .

40- **Claudia Merlini, Bruna S. Rosa, Daliana Müller, Luiz G. Ecco, Sílvia D.A.S. Ramôa, Guilherme M.O. Barra**, Polypyrrole nanoparticles coated amorphous short silica fibers: Synthesis and characterization Polymer Testing 31 (2012) 971–977

41- **I. Cucchi, A. Boschi, C. Arosio, F. Bertini , G. Freddi, M. Catellani** , Bio-based conductive composites: Preparation and properties of polypyrrole (PPy)-coated silk fabrics), Synthetic Metals 159 (2009) 246–253.

42- **Akif Kaynak, Saeed Shaikhzadeh Najar , Richard C. Foitzik** , Conducting nylon, cotton and wool yarns by continuous vapor polymerization of pyrrole, Synthetic Metals 158 (2008) 1–5.)

43- **Anne Schwarz, Jean Hakuzimana, Anna Kaczynska, Jedrzej Banaszczyk , Philippe Westbroek , Eric McAdams , Gillian Moody , Yiannis Chronis, Georgios Priniotakis, Gilbert De Mey, Dimitris Tseles, Lieva Van Langenhove,** Gold coated para-aramid yarns through electroless deposition, Surface & Coatings Technology 204 (2010) 1412–1418)

44- **M.M.B. Hasan, Ch. Cherif, A.B.M. Foisal, T. Onggar, R.D. Hund, A. Nocke**, Development of conductive coated Polyether ether ketone (PEEK)filament for structural health monitoring of composites, Composites Science and Technology 88 (2013) 76–83.

45- **Pen-Cheng Wang, Jing-Yu Yu, Kuan-Hsun Li,** All-organic polymer-dispersed liquid crystal light-valves integrated with electroactive anthraquinone-2-sulfonate-doped polypyrrole thin films as driving electrodes, Materials Chemistry and Physics 130 (2011) 1346– 1350.

46- **Z Yildiz, I Usta and A Gungor ,** Electrical properties and electromagnetic shielding effectiveness of polyester yarns with polypyrrole deposition, Textile Research Journal 82(20) 2137–2148).

47- **Daniela Negru, Cozmin-Toma Buda, Dorin, Avram.** Electrical Conductivity of Woven Fabrics Coated with Carbon Black Particles, FIBRES & TEXTILES in Eastern Europe **2012**, 20, 1(90) 53-56.)

48- **KYUNG WHA OH, KYUNG HWA HONG, SEONG HUN KIM,** Electrically Conductive Textiles by in situ Polymerization of Aniline, ELECTRICALLY CONDUCTIVE TEXTILES, 2094-2101**.**

49- **Patil, Amol J. ; Deogaonkar, Smita C.** , A novel method of in situ chemical polymerization of polyaniline for synthesis of electrically conductive cotton fabrics, TEXTILE RESEARCH JOURNAL, volume 18))

50- **Zhijian Yang, Ling Ding, Peng Wu, Yonggang Liu, Fude Nie, Fenglei Huang-** Fabrication of RDX, HMX and CL-20 based microcapsules via in situpolymerization of melamine–formaldehyde resins with reduced sensitivity, Chemical Engineering Journal Volume 268, 15 May 2015, Pages 60–66)

51- **Abdulazeez T. Lawal , Gordon G. Wallace,** Vapour phase polymerisation of conducting **WAN. M.** and non-conducting polymers: A review, Talanta 119 (2014) 133–143.)

52- **Zheng-Ming Huang, Y.-Z. Zhang, M. Kotaki, S. Ramakrishna,** A review on polymer nanofibers by electrospinning and their applications in nanocomposites , Composites Science and Technology Volume 63, Issue 15, November 2003, Pages 2223–2253).

53- **S N Patra, D Bhattacharyya , S. Ray and A. J. Easteal**, Electrospun Poly(Lactic acid) based Conducting Nanofibrous Networks, Materials Science and Engineering 4 , 2009.

54- **Audrey Frenot, IoannisS. Chronakis,** Polymer nanofibers assembled by electrospinning, Current Opinion in Colloid and Interface Science 8 (2003) 64–75).

55- **A.S. Sarac, O. Yavuz, E. Sezer**, Electrosynthesis and study of carbazole–acrylamide copolymer electrodes, Polymer 41, p 839–847 , 2000).

56- **WAN. M.** , Conducting Polymers with Micro or Nanometer Structure, Springer, 2008.

57- **FREUND M.S. , DEORE B.** , Self-doped Conducting Polymers, WILEY, 2006

58- Conducting Polymers with Micro or Nanometer Structure, Springer, 2008.

59- **Zhang X.** Controllable Synthesis of Conducting Polypyrrole Nanostructures, J. Phys. Chem. B. – (2006). – 110, 1158-1165.

60- **Lianga G.,Zhub L., Xub J., Fangb D., Baib Z., Xub W.,** (2013),Electrochimica Acta, 103,9-14.

61- **Gillian McMahon,** Analytical Instrumentation, John WILEY & Sons ,2007.

62- Characterization and Analysis of Polymers-WILEY INTERSCIENCE, 2008.

63- **Barbara Stuart-Polymer Analysis**, John WILEY & Sons, 2003).

64- **Kevin P. Menard**, Dynamical Mechanical Analysis,CRC Press, 1999).

65- **HÖHNE.G.W.H, HEMMİNGER.W.F. , FLAMMERSHEİM. H. J**. , Second Edition: Differantial Scanning Calorimetry, Springer,2003.

66- **Clademir A. BERSHTEIN, Victor M. EGOROV**, Differantial Scanning Calorimetry of Polymers, ELLIS HORWOOD, 1994).

67- **A. T. Gökçeören; C. Erbil; E. Sezer; A. S. Saraç**, Copolymers of N-vinylcarbazole with Acrylic Acid, Itaconic Acid, and Nisopropylacrylamide: Synthesis, Determination of Monomer Reactivity Ratios, and Electrochemical Properties , International Journal of Polymer Anal. Charact., 14: 140–159, 2009

68- **Esma Sezer, Özlem Yavuz, A. Sezai Saraç,** *N*-Vinylcarbazole-Acrylamide Copolymer Electrodes Electrochemical Response to Dopamine**,** *Journal of The Electrochemical Society,* 147 (10) 3771-3774 (2000)

69- **Mehmet Erginer, Esma Sezer, Belkıs Ustamehmetoğlu, Jurgen Heinze,** Voltammetric, electrochemical quartz crystal microbalance and in situ conductance studies of conducting polymers based on ethylenedioxythiophene and N-ethylcarbazole, Electrochimica Acta 67 (2012) 181– 186.

70- **A.S.Saraç, C, Erbil, B.Ustamehmetoğlu**, Polym. Bull., 33, 535-540, 1994.

71- **J.F. Feller, Y. Grohens** , Evolution of electrical properties of some conductive polymer composite textiles with organic solvent vapours diffusion, Sensors and Actuators B 97 , p 231–242 2004.

72- **Z Yildiz, I Usta and A Gungor**, Electrical properties and electromagnetic shielding effectiveness of polyester yarns with polypyrrole deposition, Textile Research Journal 82(20) 2137–2148 )

73- **Claudia Merlini, Bruna S. Rosa, Daliana Müller, Luiz G. Ecco,** Sílvia D.A.S. Ramôa, Guilherme M.O. Barra, Polypyrrole nanoparticles coated

amorphous short silica fibers: Synthesis and characterization, Polymer Testing 31, 971–977, 2012.

74- **Alessio Varesano, Barbara Antognozzi, Claudio Tonin** , Electrically conducting-adhesive coating on polyamide fabrics, Synthetic Metals 160 ,p 1683–1687, 2010)

75- **Richard C. Foitzik, Akif Kaynak*, Jens Beckmann, Frederick M. Pfeffer**, Soluble poly-3-alkylpyrrole, Synthetic Metals 155, p 185–190, 2005.

76- **Eva Hakansson , Andrew Amiet , Akif Kaynak**, Electromagnetic shielding properties of polypyrrole/polyester composites in the 1–18 GHz frequency range, Synthetic Metals 156 (2006) 917–925).

77- **Omastova M., Trchova M., Kovarova J., Stejskal J**., (2003), Synth. Metals, 138447-455.

78- **Kim B., Koncar V.,. Dufour C,** (2006), Journal of Applied Polymer Science, Vol. 101, 1252–1256.

79- **Ucar N., Demirsoy N., Onen A., Karacan I., Kızıldag N., Vurur O. F., Sezer E., Ustamehmetoglu B.,** (2015), DOI 10.1007/s10853-014-8748-4.

80- **Sandra Varnaitė,Jurgis Katunskis**, Influence of Washing on the Electric Charge Decay of Fabrics with Conductive Yarns, FIBRES & TEXTILES in Eastern Europe 2009, Vol. 17, No. 5 (76) pp. 69-75.

81- **Ustamehmetoglu B., Akar A., Kizilcan N., Kelleboz E.,** Copolymers of carbazoles and methyl ethyl ketone formaldehyde resin, Pigment & Resin Technology 41/1 25–33 (2012).

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